

SYMPOSIUM Q

Degradation Processes in Nanostructured Materials

November 28 - December 1, 2005

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* Invited paper

8:30 AM Q1.1

Electrical-current-induced degradation of carbon nanotube films: structural changes, chemical functionalization and electrical properties. Saurabh Agrawal¹, Makala S. Raghuvver¹ and G. Ramanath^{1,2}; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Max Planck Institut für Festkörperforschung, Stuttgart, Germany.

Controllably modifying the structural and chemical properties of carbon nanotubes (CNTs) is of importance to utilize them for a variety of applications ranging from active components in nanodevices and sensors, to reinforcements in nanocomposites. CNTs can carry current densities $> 10^9$ A cm⁻², making them attractive for applications as high-electromigration resistance interconnects. Here, we demonstrate the use of high current densities to weld, thin, chemically functionalize and modify the electrical properties of CNTs. Prior work has shown that injecting large current (amps) induces CNTs in vacuum to emit a stable glow due to a combination of Joule heating and photon emission, with no observable chemical changes. In our experiments, where current injection 0.1-1 A into CNT films contacted with Au electrodes is carried out in air, we observe momentary flashes due to local arcing and oxidation at high resistivity hot-spots, which ultimately results in an open circuit. Current-injection increases the structural disorder of the CNTs through defect generation, seen as an increased Raman D/G band intensity ratio. Transmission electron microscopy reveals that the CNT structure is largely intact except for local CNT thinning and fissures. In addition, CNT-CNT welds are formed between overlapping CNTs, suggesting that the high resistance at the points of overlap serve as hot spots for arcing. The current-injected CNTs are rendered hydrophilic as seen from infrared absorption and X-ray photoelectron spectra showing signatures corresponding to O-H, C=O, C=C, and O=C-OH moieties, not detectable in as-prepared CNTs. These results suggest that current-injection-induced dangling bonds generated at the hot-spots serve as fertile sites for functionalization through reaction with water and oxygen. Prior to open circuit failure, the net conductance of the CNT film increases upon current injection, contrary to the conductance decrease expected due to defect creation and functionalization. Thus, during the initial stages of current injection, the creation of low-resistance CNT-CNT welds dominates over increased carrier scattering at defects. Our findings hold promise to scalably produce functionalized CNT networks from overlapping CNT assemblies for applications in CNT-based devices and composites.

8:45 AM *Q1.2

Multi-scale Modeling of Carbon Nanotubes in Graphite-Epoxy Composites. S. J. V. Frankland¹, J. C. Riddick² and T. S. Gates³; ¹National Institute of Aerospace, Hampton, Virginia; ²U. S. Army Research Laboratory, Hampton, Virginia; ³NASA Langley Research Center, Hampton, Virginia.

Because of the limited production and difficulty in processing carbon nanotube polymer composites, there is interest in utilizing carbon nanotubes in critical areas of traditional structural materials to improve their mechanical properties. In the present work, multi-scale modeling efforts are underway to address the effect of carbon nanotube on the constitutive properties of graphite-epoxy laminates. Molecular dynamics simulations (MD) are performed of a carbon nanotube epoxy composite in the region of a graphitic surface. The MD simulations are used in conjunction with the equivalent continuum (EC) approach to determine the constitutive properties. The MD/EC method will be used in a parametric study to examine the relative effect of nanotube concentration and orientation at the graphitic surface.

9:15 AM Q1.3

Raman and Electron Spin Resonance Investigations of as Prepared and Thermal Annealed Cluster Beam Deposited Carbon Thin Films. Orazio Puglisi¹, Giuseppe Compagnini¹ and Mircea Chipara²; ¹Chemistry Department, Indiana University, Bloomington, Indiana; ²Department of Chemistry, University of Indiana, Bloomington, Indiana.

Nanostructured amorphous carbon thin films have been deposited by a Low Energy Carbon Cluster Beam Deposition technique. These samples have been characterized by Raman spectroscopy and Electron Spin Resonance (ESR) in order to study the correlation between their structure and the sp² related defects. The ESR spectra were recorded by using a Bruker EMX spectrometer, operating in X-band, in the temperature range 200 K to 400 K. A high density of ESR active

paramagnetic centres located $g=2.0028$ has been observed in the as deposited samples. These centres are randomly distributed and correlated with the nanosized nature of the investigated system. Resonance lines were accurately fitted by a single narrow Lorentzian line. The absence of the resonance line asymmetry, typical for the ESR spectra of conducting materials, confirms the small size of carbon nanoclusters and indicates poor electrical contacts between them. The resonance line parameters (position, intensity, and width) are not affected by the orientation of the carbon cluster film relative to the direction of the external magnetic field. The evolution of the ESR signal upon thermal treatments follows the increase in the sp² average domain size as revealed by Raman spectroscopy.

10:00 AM *Q1.4

Preparation of Polystyrene and Polycarbonate Carbon Nanofiber Composites. Yijin Xu, Bernadette Higgins and Bill Brittain; Polymer Science, The University of Akron, Akron, Ohio.

In this presentation, we will present results on the incorporation of carbon nanofibers (CNF) into polystyrene (PS) and polycarbonate (PC) matrixes. Thermal properties were characterized by DSC and TGA, while morphologies of the nanocomposites were studied by SEM. The PS-CNF nanocomposites were synthesized by a bottom-up method through electrostatic assembly. First, a cationic PS latex was synthesized by a conventional emulsion polymerization. The latex was mixed with an aqueous suspension of oxidized CNFs. PS-CNF nanocomposites were obtained by heterocoagulation due to the electrostatic interaction between cationic PS latex and anionic CNF. Electrical resistivity results showed that the percolation threshold in our PS-CNF nanocomposites was below 2 wt% (1 vol%). This low percolation threshold is related to the dispersion, and thus indicating a superior network formation of CNF in PS matrix. For the PC-CNF nanocomposites, we used a low shear method that exploited the in-situ polymerization of cyclic oligomeric carbonates. The composites exhibit minimal aggregation of the carbon nanofibers even at high weight percents. The polycarbonate/CNF composites exhibited an electrical conductivity percolation threshold of 6.3 wt% which is higher compared with similar PC-CNF composites prepared by high shear methods. The composites show an increase in thermal stability of 40°C as the CNF loading increases from 0 to 9 wt %.

10:30 AM Q1.5

Mechanical Degradation of Carbon Nanotubes: ESR Investigations. Magdalena D. Chipara³, Akos Kukovecz², Tímea Kanyó², Zoltan Kanyó², Imre Kiricsi², Michelle L. Borden², Emma S. Shansky², Jeffrey M. Zaleski¹, David Dye¹ and Mircea Chipara¹; ¹Chemistry Department, Indiana University, Bloomington, Indiana; ²Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary; ³PartTec, Bloomington, Indiana.

The outstanding physical (Young modulus, tensile strength, thermal conductivity, and electrical conductivity) and chemical properties of carbon nanotubes (CNTs), triggered much theoretical and experimental research. For certain applications such as gas storage and absorption, short opened end CNTs are required. Mechanical milling and sonication are the most frequently utilized techniques to cut long CNTs into short ones. The energetic ball milling has been performed by using two cylindrical drums filled with multiwalled carbon nanotubes powder, placed into a vibrational mill horizontally and driven with an eccentric shaft at 50 Hz. The milling time was ranging between 0 hours and 200 hours. The sonication time was ranging between 0 hours and 200 hours, at a sonication power of about 50 W. Electron spin resonance (ESR) investigations on milled and sonicated multiwalled carbon nanotubes have been performed by using a Bruker EMX spectrometer operating in X-band (about 9 GHz). The dependence of resonance line parameters (resonance line position, resonance line amplitude, resonance line shape, and double integral of the resonance line) on the sonication and milling time has been investigated in detail. Complex similar resonance spectra have been recorded in both pristine and milled samples. These spectra have been assigned to the convolution of a wide resonance line originating from magnetic impurities (catalysts residues) with a broad resonance line assigned to uncoupled electronic spins delocalized over the conducting domains of CNTs. Accordingly, the as recorded resonance spectra were deconvoluted into two Lorentzian-like components and accurately simulated. The details of the recorded resonance spectrum prevented us from an accurate estimation of the wide line parameters. The parameters of the broad resonance lines have been accurately determined. It was observed that the parameters of the broad line are affected by milling duration. That allowed us to correlate these data with the structural modifications of carbon nanotubes, as revealed by transmission electron microscopy [1, 2]. No new resonance line has been observed in milled CNTs. The experimental data obtained by ESR spectroscopy are compared to Raman spectroscopy data. References 1. Z. Konya, J. Zhu, K. Niesz, D. Mehn, I. Kiricsi, Carbon, 42, 2001-2008, 2004 2. A. Kukovecz, T. Kanio, Z. Konya, I. Kiricsi, Carbon, 43, 994-1000, 2005.

10:45 AM *Q1.6

Degradation Behavior of Polymer-Derived CNT/Ceramic Matrix Composite Materials. Michael Scheffler, Craig S. Terry, John Morris and Rajendra K. Bordia; Department of Materials Science and Engineering, University of Washington, Seattle, Washington.

Recently, we have demonstrated a new approach of in situ formation of multiwall carbon nanotubes (CNTs) in a polymer derived ceramic matrix at comparatively low temperatures. The method combines spaceholder techniques for pore generation and conversion of releasing gases in transition metal doped preceramic polymers into CNTs. Processing was carried out in the temperature range from 500 to 1200 degree C in inert atmosphere and the resulting products were characterized by x-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transition electron microscopy (TEM) and specific surface area analysis (BET). CNTs were found to be formed in the pores which have been generated by the polystyrene spaceholders. With this technique both isolated, CNT-containing pores and a transient, open-porous networks can be formed as controlled by the volume fraction of spaceholders. Degradation experiments were carried out by annealing in argon atmosphere at temperatures above 1000 degree C and in air in the temperature range between 400 and 800 degree C over periods of days. The resulting products were characterized by weight loss measurement, SEM and XRD analysis. It was found that the CNTs enclosed in pores withstand significantly higher temperatures in air as compared to CNTs located in open pores. The results were discussed with respect to the annealing time and a model for the oxidation kinetics was established.

11:15 AM Q1.7

Photo-oxidation of Singlewalled Carbon Nanotubes. B. Parekh¹, Thomas Debies², C. M. Evans³, B. J. Landi³, R. P. Raffaele³ and Gerald A. Takacs¹; ¹Department of Chemistry, Center for Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York; ²Xerox Corporation, Webster, New York; ³Nanopower Research Laboratories, Rochester Institute of Technology, Rochester, New York.

The effect of UV- and VUV-assisted photo-oxidation on the structure and electronic properties of single wall carbon nanotubes (SWNTs) has been investigated. Photo-oxidation occurred by the following techniques: (1) atmospheric oxygen pressure using low-pressure Hg lamps ($\lambda = 253.7/184.9$ nm), (2) low oxygen pressure with emission downstream from an Ar microwave plasma ($\lambda = 106.7/104.8$ nm), and (3) high pressures of He in a rotating d.c. arc that was designed to produce a spectral continuum from He excimers ($\lambda = 58 - 110$ nm) [1]. The resulting photo-oxidized materials were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Raman and optical absorption spectroscopy as a function of treatment method and experimental conditions. The oxidative stability and extent of surface modification on high purity SWNT papers will be presented. In addition, the utilization of a controlled procedure for introduction of select oxygenated functional groups (aldehydes, ketones, carboxylic acids, etc.) is demonstrated in the context of SWNT functionalization for covalent chemical reactions. * To whom correspondence should be addressed. Phone: 585-475-2047, Fax: 585-475-7800. E-mail address: gatsch@rit.edu [1] S. Zheng, A. Entenberg, G. A. Takacs, F. D. Egitto and L. J. Matienzo, J. Adhesion Sci. Technol. 17, 1801 - 1813 (2003).

11:30 AM *Q1.8

Radiation, Annealing, and Mechanical Strain Contributions to the Degradation of Carbon Nanotube Nanocomposites. J. M. Zaleski, Magdalena D. Chipara, Michelle Borden and David F. Dye; Chemistry, Indiana University, Bloomington, Indiana.

Carbon nanotubes are characterized by large Young moduli and mechanical strength, high thermal conductivities, large electrical conductivity, and small energy gaps. The intimate connection between carbon nanotube morphology (chirality, size) and their physical properties is widely recognized. However, these structures are modified by temperature, mechanical stress, and radiation effects. These physical hazards inhibit application of carbon nanotube nanocomposites and thus an understanding of their behavior under these ranging conditions is important. Moreover, the functionalization of carbon nanotubes can be accelerated by sonication and microwave radiation, but prolong exposure to these conditions can also lead to structural damage and degradation of the physical/mechanical properties of the resulting nanocomposites. Nanocomposite materials containing nanotubes dispersed in polymeric matrices are characterized by improved and/or controlled physical properties (mechanical, thermal, and optical). Complex degradation processes have been reported in such composites when subjected to mechanical stresses, temperature, and ionizing radiation. Using Raman spectroscopy, thermal analysis, and electron spin resonance, we have

investigated the structural origins of nanotube/nanocomposite degradation caused by these hazards. For carbon nanotubes, the primary degradation is associated with tube fracture and localized defects, while for nanocomposite materials, breakdown is related to nanotube/polymer adhesion. This is an important structural variable that determines the mechanical lifetime of carbon nanotubes based composites. The spectroscopic and mechanical data underlying these themes will be presented and correlated to structure-function conclusions.

SESSION Q2: Nanotube & Radiation
Chairs: Enrique Barrera and Mircea Chipara
Monday Afternoon, November 28, 2005
Room 209 (Hynes)

1:30 PM *Q2.1

The Effect of Microwave Radiation on the Carbon Nanofiber/Polymer Composite. Shuying Yang, Arturo Fuentes, Rogelio Benitez and Karen Lozano; Mechanical Engineering, University of Texas Pan American, Edinburg, Texas.

Carbon nanofiber and carbon nanotube reinforced polymer composites have shown promise due to their enhanced mechanical, electrical, and thermophysical properties. An important area of study focuses on the electromagnetic interference shielding effectiveness, due to the recent increase in electronic devices (commercial, military, and scientific) that either utilize or are exposed to electromagnetic radiations. Electromagnetic radiations are known to affect dielectric materials through polarization mechanisms. This study focuses on analyzing the degradation of nanofiber reinforced polymer composites exposed to microwave radiations. This type of composites present intrinsic heating uniformity problems which cause localized degradation of the dielectric material exposed to microwave radiation. The effect of high power microwave radiation on the physical integrity of the composites via mechanical and thermophysical analysis will be presented.

2:00 PM *Q2.2

Irradiation Induced Surface Modifications in Multifunctional Nanostructured Carbons. Sanju Gupta, Physics and Materials Science, Missouri State University, Springfield, Missouri.

Severe environmental tolerability is the prime factor in the development of novel space materials exhibiting excellent physical properties accompanied by lightweight, reusability, and multifunctional capabilities. Diamond is known for its reputation being radiation hard besides a range of outstanding properties and hence it is preferable in harsh environments. Carbon nanotubes are also of great interest because of several unsurpassable physical properties and it needs to be shown that they are physically stable and structurally unaltered when subjected to irradiation. Films of micro-, nanocrystalline diamond and carbon nanotubes were deposited by microwave CVD technique. While diamond films were submitted to gamma radiation (1, 5, and 20 Mrads), the carbon nanotubes were subjected to electron-beam irradiation to study their effects on structure and the corresponding physical properties to establish property-structure correlation [1]. Microstructural and physical properties characterizations prior to and post-irradiation include scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), field emission (FE), and high-resolution transmission electron microscopy (HRTEM). Dramatic improvement in the field emission properties for microcrystalline diamond and relatively small but systematic behavior for nanocrystalline diamond with increasing radiation dose is discussed in terms of critical role of defects. These results are also discussed in terms of sp^3 , $sp^{(2+d)}$ \leftrightarrow sp^2 C inter-conversion [1]. The influence of electron beam irradiation on both single- and multi-walled nanotube films was investigated by subjecting them continuously to constant energy of 50 - 100 keV for a few hours and were analyzed using abovementioned characterization tools. Experimental studies show multi-walled tends to be relatively more robust than those of single-walled. Increased exposure on an individual bundle of single-wall nanotube promoted graphitization, pinching, and crosslinking forming intra-molecular junction (IMJ), possibly through aggregates of amorphous carbon [1], revealed through SEM and TEM. Formation of novel nanostructures (nano-ring and helix-like) due to irradiation are also observed. The possible radiation mechanism will be briefly discussed. More importantly, they provided a contrasting comparison between semiconducting (single-wall) and metallic (multiwall) nanotubes and gleam on a regime of possible relevance for short-term space missions. [1] S. Gupta, B. L. Weiss, B. R. Weiner, L. Pillone, A. Badzian, and G. Morell, J. Appl. Phys. 92, 3311 (2002); S. Gupta, R. J. Patel, N. D. Smith, Mater. Res. Soc. Symp. Proc. 851, NN6.3-NN6.10 (2004); S. Gupta, R. J. Patel, N. D. Smith, Y. Y. Wang, R. E. Giedd, J. Appl. Phys. (2005) (submitted).

3:30 PM Q2.3

Effects of MeV Ions on Thermal Stability of Single Walled Carbon Nanotubes. Ananta Raj Adhikari¹, Membing Huang¹,

Pullickel Ajayan² and Hassaram Bakhrui¹; ¹Nanoscale Science and Engineering, State University of New York, Albany, New York; ²Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

The properties of carbon nanotubes (CNTs) are closely dependent on their structures, and therefore may be tailored by controllably introducing defects in the nanotube systems. In this work, we investigate the effects of energetic ions (H⁺ and He⁺) on the thermal stability of single wall nanotubes (SWNTs) against oxidation in air. SWNTs were irradiated with ions of energy in MeV to various doses in the range of 10¹³ - 10¹⁶ cm⁻². Thermal oxidation of CNTs was performed in air at temperatures 200-700 degree centigrade. Thermogravimetric analysis (TGA) was used to determine the loss of CNT masses as a result of oxidation processes. As opposed to the case of pristine SWNTs for which the temperature (Tm) corresponding to maximum oxidation rate was found to be 495 degree centigrade, ion beam processing could significantly enhance the thermal stability of nanotubes, e.g., Tm increases by about 30 degree centigrade from H ion implantation (at the ion dose of 10¹⁵ cm⁻²) and 17 degree centigrade for He ion implantation (at the ion dose of 10¹³ cm⁻²). The activation energies for thermal oxidation under various conditions were also extracted from TGA data, with values ranging from 1.13 eV (for pristine SWNTs) to 1.37 eV, depending on ion doses and species. Raman spectroscopy was used to determine the characteristics of the G band (C-C stretching mode) and D band (disorder induced mode) in CNTs. The work suggests that the SWNTs modifies to more stable structure (may be cross-linked SWNTs) preserving its originality at small doses. Once the number of defects exceeds some critical value (depending on the types of bombarding ion) the bonding energy in CNTs then weakened, leading to the reduced thermal stability of CNTs against oxidation.

3:45 PM *Q2.4

Degradation Studies on Carbon Nanotube Materials from Radiation Relevant to the Space Environment.

Richard Wilkins¹, Merlyn X. Pulikkathara², Valery N. Khabashesku² and E. V. Barrera³; ¹NASA Center for Applied Radiation Research, Prairie View A&M University, Prairie View, Texas; ²Department of Chemistry, Rice University, Houston, Texas; ³Department of Mechanical and Material Science, Rice University, Houston, Texas.

Materials using the exceptional properties of carbon nanotubes are under scrutiny by the aerospace community for a variety of applications. These materials will operate in a hostile environment that will include high-energy particulate radiation from the sun and from galactic cosmic rays (GCR). The degradation characteristics of these materials are important for the development of materials for the aerospace environment. We will present highlights of recent results on the effects of high energy particulate radiation on the material properties of carbon nanotubes and nano-composites. The radiation sources included in the present work are heavy ions of various linear energy transfer (LET) values. The purpose of these experiments is to study the dependence of energy deposition on the radiation degradation on the materials. The LET values are commensurate with heavy ions of the GCR spectrum. Materials are characterized pre- and post-irradiation and/or against non-irradiated controls. We will discuss the implications of the degradation studies as related to aerospace applications of carbon nanotube materials.

4:15 PM *Q2.5

Effects of Space Environments on Nanotube Polymer Nanocomposites. Cheol Park¹, Jinho Kang¹, Kyo D. Song², Sharon E. Lowther³ and Joycelyn S. Harrison³; ¹National Institute of Aerospace, Hampton, Virginia; ²Norfolk State University, Norfolk, Virginia; ³Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia.

A series of high performance polymers were developed for use as sensing/actuating components in future space vehicles and astronaut suits. Carbon nanotubes (CNTs) were incorporated to form a composite material in an attempt to enhance the multifunctionality of these polymers while improving their mechanical, thermal, and electronic characteristics. These multifunctional structural materials are expected to have a prolonged exposure in harsh space environments such as high-energy protons and electrons, ultraviolet radiation, atomic oxygen, high and low thermal excursions, hard vacuum, galactic cosmic radiation, micrometeors, and man-made debris. These effects often lead to significant degradation of their functionalities. In this presentation, the effects of simulated hostile space environments on the multifunctionalities of the CNT polymer composites will be discussed. The sensing/actuating characteristics as

well as mechanical properties of the composites will be assessed before and after exposing to atomic oxygen, UV radiation, and/or high thermal fluctuations for extended period of times to understand degradation process. In addition, a series of these multifunctional polymer composites will be delivered into space for exposure on the exterior of the International Space Station as a part of MISSE (Materials International Space Station Experiment) program sponsored by NASA. These materials will be retrieved after scheduled long-term exposures for further assessments. Results obtained from the MISSE program in conjunction with the simulated space environmental tests will provide crucial information to design desirable space materials that can survive during long-term space exploration in near future.

SESSION Q3: Carbon Nanotubes II
Chairs: Cheol Park and Jeffrey M. Zaleski
Tuesday Morning, November 29, 2005
Room 209 (Hynes)

8:30 AM *Q3.1

Abstract Not Available E. V. Barrera

9:00 AM *Q3.2

Radiation Effects on Glassy Polymeric Carbon.

A. Leslie Evelyn¹, Robert L. Zimmerman¹, Marcello G. Rodrigues², Claudiu Muntele¹, Iulia Muntele¹ and Daryush Ila¹; ¹Physics, Alabama A&M University, Normal, Alabama; ²Department of Physics and Mathematics, University of Sao Paulo, Ribeirao Preto/SP, Sao Paulo, Brazil.

Glassy polymeric carbon (GPC) is made from cured phenolic resins and has a high chemical inertness that has resulted in the material being used in a wide variety of applications, such as a biomaterial in medicine for the manufacture of heart valves. We have used the interaction of low and high-energy ions with both partially and fully cured phenolic resins to modify the properties of the GPC. Samples were bombarded with energetic ions, and post ion bombardment characterization showed changes in their mechanical, electrical and chemical structures. We will report on the techniques used and the corresponding results of the radiation effects on the GPC.

10:00 AM Q3.3

Effect of Nanoparticles in the Thermal Stability of Polymers.

Juan Gonzalez-Irun^{3,2}, Ana Garcia¹, Mircea Chipara¹, Ramon Artiaga¹ and Luis Liz-Marzan²; ¹Ingenieria Industrial II, Universidade da Coruna, Ferrol, Spain; ²Quimica Fisica, Universidade de Vigo, Vigo, Spain; ³Mechanical Engineering, University of New Orleans, New Orleans, Louisiana; ⁴Indiana University Cyclotron Facility, Bloomington, Indiana.

The use of nanoparticles as filler-reinforcement of polymer matrix is of high interest since an increase of the mechanical properties of polymeric matrices was reported for low concentrations of nanotubes. The thermal properties of the polymeric matrix (glass transition temperature, melting temperature, and crystallization temperature) are affected by the interactions between nanoparticles and the macromolecular chain. For many industrial applications, where the material may be subjected to high temperatures, it is also important to know the effect of nanoparticles on the thermal stability of the polymeric matrix. It is generally accepted that an increase in the inorganic filler content results in higher thermal stability. Nevertheless, it has been also reported that at certain temperatures the nanocomposite may show higher degradation rate than the pristine polymer. The effect of nanoparticle content and nanoparticle features in the thermal stability of different polymers has been investigated by dynamic thermo gravimetric analysis. Silica nanospheres with narrow particle size distribution, carbon nanotubes and nanoclays were included, by different ways, in poly-(methyl methacrylate) and styrene-isobutene-styrene block copolymers. The experiments were carried out both in air and inert atmosphere with nanocomposites and with unfilled polymers. Finally, the plots were fitted to a degradation model in order to better understand the degradation processes.

10:15 AM Q3.4

ESR Investigations on Carbon Nanofibers. Mircea Chipara¹,

Robert Hauge², Hua Fan³, Richard Booker², Haiqing Peng², Wen-Fang Hwang², Jeffrey M. Zaleski¹ and Richard E. Smalley³; ¹Chemistry Department, Indiana University, Bloomington, Indiana; ²Department of Chemistry, Rice University, Houston, Texas; ³Physics and Astronomy Department, Rice University, Houston, Texas.

Small amounts of carbon nanotubes (CNTs) improve the physical properties (mostly mechanical and thermal) and deliver new features (antistatic, conducting, or shielding) to insulating polymeric matrices.

These changes triggered the research on composite materials obtained by dispersing CNTs within polymeric matrices. Carbon nanofiber (CNF) is a cheap alternative to polymer-CNTs composites. Crude Carbon Nanofibers (CNFs) obtained from purified HiPco SWNT [1] were investigated by electron spin resonance (ESR) spectroscopy using a Bruker EMX spectrometer operating in X-band (about 9.0 GHz). The dependence of the resonance line parameters (resonance line position, resonance line amplitude, resonance line width, double integral of the resonance line, and resonance line shape) on the relative orientation of CNFs relative to the direction of the applied external magnetic field has been analyzed. The temperature dependence of the above mentioned resonance line parameters has been explored in (the range 200 K to 400 K). The ESR spectra of crude CNFs consist of a broad, intense, and asymmetric line. In the low magnetic wing of this line a faint broad resonance due to magnetic impurities has been observed. The distortion of the symmetrical resonance line reflects the damping of the electromagnetic field within the conducting domains. For carbon nanotubes (CNTs) the typical skin depth is of the order of about 100 nm. Hence, the theory of the anomalous skin effect [2] has been used to simulate the resonance line shape (assuming that CNTs are oriented along the microwave field). The recorded spectrum is more complex and cannot be accurately fitted by the line shape derived within the anomalous skin effect approximation. The resonance line shape of crude CNFs was accurately described by a convolution of two Dysonian lines (and an additional Lorentzian line assigned to magnetic impurities). Both Dysonian lines are located near $g=2.00$ and have resonance linewidths of about 6 mT and 24 mT, respectively (at room temperature). The broad line was tentatively assigned to uncoupled electrons delocalized over the conducting domains of CNTs. This line reflects the weak metallic properties of crude CNTs derived from the p doping (presumably due to bisulfate ions [1]) of nanotubes. The resonance line is broadened by the interaction of conducting electrons with paramagnetic or magnetic impurities. The nature of the second Dysonian line has not yet been identified. It may be tentatively assigned to graphite like structure. This research is funded by ONR N000014-01-0789 and STTR US Army grant # A2-1299 (03-T16). References 1. Zhou, W.; Vavro, J.; Guthy, C.; Winey, K. I.; Fischer, J. E.; Ericson, L. M.; Ramesh, S.; Saini, R.; Davis, V. A.; Kitrell, C.; Pasquali, M.; Hauge, R. H.; Smalley, R. E., *J. Appl. Phys.*, 2004, 95, 649. 2. Feher, G.; Kip, A. F., *Phys. Rev.*, 1955, 98, 337.

10:30 AM *Q3.5

Polymer Structure, Dynamics, and Reactivity in Thin Films and Under Nanoscale Confinement. Steven J. Sibener, The James Franck Institute, The University of Chicago, Chicago, Illinois.

The formation, physical characterization, dynamical properties, and reactivity of thin films are central to our understanding of interfacial science including nanoscale systems. This presentation will focus on the characteristics of organic and hierarchically assembled inorganic/organic hybrid films, in free thin films as well as under nanoscale confinement. The presentation will begin with a discussion of issues pertaining to defect mobility and thermal annealing, spatial organization, and the prospect for functional decoration of diblock copolymer surface structures. This effort has demonstrated that atomic force microscopy imaging can be used in a time-lapse manner to track the interactions of topological defects. Combining rules for various dislocation and disclination pairs have been established. Strong polymer alignment has been realized in dewetted annular structures and on lithographically generated grating substrates in which intentionally selected depths and widths have been used to guide the assembly of highly-aligned polymeric interfaces under either kinetic or thermodynamic control. The phase-separated 25 nm diblock cylinders geometrically aligned by this procedure are essentially defect free, exhibit remarkable spatial coherence spanning microns, and are structurally compliant as is characteristic of "soft" organic systems. Recent activities have focussed on guiding the formation of phase separated polymeric structures in complex geometries, as well as the hierarchical decoration of these thin film materials with magnetic nanoparticles. The latter part of this presentation will describe incisive experiments which utilize inelastic neutral atom scattering to probe the surface molecular dynamics of polymeric thin films. These measurements are important as they characterize the atomic-level surface vibrational dynamics of polymers, information needed for understanding gas-surface collisional energy transfer. Such measurements also probe how the properties of nanoscale thin films may differ from those characteristic of bulk materials. Finally, studies of polymer surface degradation and reactivity involving VUV illumination and reactions due to $O(^3P)$ atomic oxygen will be described. It is with pleasure that I acknowledge my collaborators: K. Gibson, N. Isa, S. Darling, N. Yufa, A. Cisse, S. Bader, X.-M. Lin, K. Nicholson, T. Minton, Q. Zheng, I. Popova, J. Hahm, D. Sundrani, D.-C. Lee, and L. Yu.

11:00 AM *Q3.6

Nanotubes and Nanoclays Related Polymer Composites.

Alan Kin-tak Lau, Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong.

The development of activities in the area of nanoscience and nanomaterials is increasing at a tremendous speed. This fast evolution may change radically the ways in which materials are made, resulting in new materials with improved or/and new properties. The ability to manipulate the matter at atomic and molecular level resulted in materials and structures that have unique functionalities and characteristics. The basic premise is that novel or improved functionalities (physical, chemical, and biological) can be designed for advanced nano and innovative composites by employing a suitable nanoscale or other fine scale architecture elements that control the corresponding properties. The design of nanostructured and innovative materials and composites is not just a refinement of the polycrystalline microstructural scale, but rather an exploration of novel processing routes for synthesizing, characterizing, and controlling the structure of novel materials and composites. For instances, the loading of polymeric matrices (epoxy-, polyester, polyurethane (PU) and polycarbonate (PC)) with carbon nanotubes, in straight, coiled and bamboo forms enhances the toughness of matrix without a substantial increase of its weight [1-2]. Nanoclay, a cheap and fine layer silicate, enhances the thermal stability and glass transition temperature (T_g) of PU, are used to make clay-polyolefin nanocomposite (called Nanocor) that is being introduced on some GM models. The parts are stiffer, lighter, and less brittle at low temperatures than conventional polyolefin composites made with fillers such as talc. The overall market for nanoclays is small, but could jump rapidly as more applications are commercialized [3]. Exfoliated clay also improves the hardness and T_g of polymer-based materials, in which the applications of the polymer at higher servicing temperature condition [4]. This lecture will be specially focused on introducing all recent significant research findings in different engineering, chemistry and physics areas from the worlds leading researchers and to provide an opportunity to explore ideas towards the product design and development industry. Several recent products, made by nano-structural materials will be detailed discussed. References: 1. Gou J and Lau KT. Modeling and Simulation of Carbon Nanotube/Polymer Composites. A chapter in The Handbook of Theoretical and Computational Nanotechnology, to be published by American Scientific Publishers in 2005, edited by Michael Rieth and Wolfram Schommers. 2. Lau KT and Hui D. The Revolutionary Creation of New Advanced Materials - Carbon Nanotube Composites. Composite Part B: Engineering, 2002; 33: 263-277. 3. B. Wetzel, F. Hauptert, M. Q. Zhang, "Epoxy nanocomposites with high mechanical and tribological performance", *Comp. Sci. and Tech.* 63 (2003) 2055-2067. 4. Lam CK, Cheung HY, Ling HY and Lau KT. Effect of ultrasonic sonication in nanoclay clusters of nanoclay/epoxy composites. *Materials Letters*. 2005; 59(11): 1369-1372.

11:30 AM *Q3.7

Abstract Not Available D. Hui

SESSION Q4: Nanocomposites
Chairs: Rajendra Bordia and Frank Jones
Tuesday Afternoon, November 29, 2005
Room 209 (Hynes)

1:30 PM *Q4.1

Thermal and Gamma Radiation Stability of Polysiloxanes Incorporating Silica and Nano-scale Pseudo Fillers.

Mogon Patel¹, Julian James Murphy¹, Anthony Swain¹, Robert Maxwell² and Sarah Chinn²; ¹Atomic Weapons Establishment, Reading, United Kingdom; ²Lawrence Livermore National Laboratory, Livermore, California.

The use of internal nano-scale molecular filler molecules such as Polyhedral oligomeric silsesquioxane (POSS), carborane cage units and precipitated tin oxides, yields reinforcing regions comparable in size to those of the molecular dimensions of the polymer. This potentially imparts significant improvements to the engineering and mechanical properties, even when the material is subjected to elevated temperatures. In conventional, silica filled systems, effects associated with water at the polymer-filler interface complicate ageing behaviour in siloxanes making it difficult to predict how properties will change over time. In nano-composite materials the properties of the system are not as influenced by water so ageing behaviour is simplified. Polysiloxane polymers can be readily analysed by variety of nuclear magnetic resonance (NMR) techniques. These provide an insight into segmental chain dynamics and polymer viscoelastic properties. In this paper an overview of work performed on a variety of filled polysiloxane materials is given. The property enhancement effects of POSS and the enhanced stability offered by the incorporation of carborane units are discussed. The complexities of polymer-particle

interactions, including evidence for radiation induced paramagnetic species confined in the filler matrix will be reported. An outline of data obtained from a range of analytical techniques including, high resolution proton NMR, Electron spin resonance (ESR), Mossbauer spectroscopy, thermomechanical analysis, ammonia modified solvent swell and differential Scanning Calorimeter (DSC) will be given.

2:00 PM *Q4.2

Fire Retardancy and Morphology of Nylon 6-Clay Nanocomposite Compositions. Prabir K Patra¹, Kadiravan Shanmuganathan¹, Sandeep Razdan², Qinguo Fan¹, Yong Kim¹, Paul Calvert¹ and Steve Warner¹; ¹Textile Sciences, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts; ²Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We examined the effect of layered silicate concentration and the influence of intercalation or delamination of organically modified clay on the evolution of morphology in nylon 6 nanocomposites and its thermal and flammability behavior. We used Zinc borate along with layered silicate with an aim to achieve synergistic effect in terms of flame retardancy of the nanocomposites. Wide angle x-ray diffraction (WAXD) patterns and TEM images of the nanocomposites reveal a well intercalated /delaminated clay morphology with 2.5% and 5% clay however, with 10% clay the extent of intercalation is lower. The effect of clay concentration and different levels of intercalation on the crystalline morphology of nylon 6 was studied by differential scanning calorimetry (DSC). While neat nylon 6 showed a main melting peak at 221 deg C and a shoulder at 213 deg C, corresponding to α and β phases respectively, the nanocomposites revealed three melting peaks at 203 deg C, 213 deg C and 220 deg C which could be attributed to β , α and γ phases respectively. The area under the peaks changes with clay concentration. Differential thermo gravimetric analysis (DTGA) indicates that the peak decomposition temperature is not affected by the addition of clay but the rate of weight loss decreases with increasing clay concentration. The onset of decomposition at 5% wt loss temperature decreases by 20 deg C with 10% clay concentration. However, the addition of 5% Zinc borate and 5% clay in combination minimizes the degradation effect of nylon 6 as compared to 10% clay. The burning behavior of the nanocomposite films of 0.5 mm thickness under vertical condition changed with additive concentration. The nanocomposites with 2.5% and 5% clay burnt almost similarly as neat nylon 6 but the dripping was reduced. The 10% clay nanocomposite sample burnt without dripping and the burning time was 4 times longer than neat polymer. The burning time of 5% Zinc borate / 5% clay nanocomposite sample was longer than 10% clay nanocomposite sample which could be attributed to different char morphology among other factors. These observations indicate the minimum additive level required to modify the burning behavior of thin films under vertical condition. Scanning electron microscopy (SEM) images of the char surface and cross section reveals an integrated layer with density gradient from the surface to the bulk. We anticipated entrapment of polymer fragments between the densely accumulated clay platelets on both surfaces of char. Fourier transform infrared Spectroscopy (FTIR) of the Zinc borate nanocomposite char shows the presence of alkanes, alkenes and amides which indicates possible unburnt polymer recession within the shielded char.

3:30 PM Q4.3

Nanoparticle Networks Lead to Improved Flammability Properties of Polymer Nanocomposites. Fangming Du¹, Takashi Kashiwagi², John E. Fischer³ and Karen I. Winey^{3,1}; ¹Chemical and Biomolecular Department, University of Pennsylvania, Philadelphia, Pennsylvania; ²National Institute of Standards and Technology, Gaithersburg, Maryland; ³Department of Material Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Recently, nanoparticle fillers have been highly attractive for being alternative flame-retardant (FR) additives to replace some effective halogenated FR additives because the nanoparticles simultaneously improve both the physical and flammability properties of polymers. These nanofillers form a network-structured protective layer covering the sample surface and act as a heat shield for the virgin polymer below the layer, which results in a significant reduction in the heat release rate. We chose four carbon-based nanoparticles, single wall carbon nanotube (SWNT), multi wall carbon nanotube (MWNT), carbon nanofiber (CNF), and carbon black (CB) to systematically study the effects of the filler size, type, and loading on their polymer nanocomposites flammability and rheological properties. These nanocomposites show significant improvement in flammability and exhibit solid-like rheological behaviors due to the formation of nanofiller networks. Our results also show that the network in the nanocomposite is formed with 0.5wt% SWNT, 1wt% MWNT, or 4wt% CNF, while the addition of CB fail to form a network at concentrations \leq 4wt%.

3:45 PM *Q4.4

Modelling of Crack Propagation Due to Localized Embrittling Conditions at Crack Tips. Santiago A. Serebrinsky¹, Carter A.

Emily² and Michael Ortiz¹; ¹Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California; ²Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

Under suitable environmental conditions, most materials (if not all) can undergo environment-assisted cracking (EAC). The local environmental and material conditions in a very small region close to the crack tip are essential for EAC to develop. We present a model of hydrogen embrittlement (HE) -a particular instance of EAC- based on cohesive theories of fracture, aimed at simulating crack propagation. The essential ingredients of the model are: (i) a cohesive law dependent on hydrogen surface coverage that is calculated from first principles; (ii) a stress-assisted diffusion equation for hydrogen transport; (iii) a static continuum analysis of crack growth including plasticity; and (iv) the Langmuir relation determining the impurity coverage from its bulk concentration. The effect of several system parameters is analyzed. Essential qualitative and quantitative features of crack propagation in high strength steels (HSS) are reproduced, namely: (i) the existence of a threshold stress intensity factor and a plateau crack velocity, and their dependence on yield strength; (ii) the existence of a time to initiation and its dependence on yield strength and stress intensity factor; (iii) finite crack jump at initiation; (iv) intermittent crack growth under certain conditions; (v) the effect of the environmental hydrogen activity on the threshold stress intensity factor; and (vi) the effect of temperature on plateau crack velocity in the low-temperature range. The predictions of the model suggest that hydrogen-induced degradation of cohesion is a likely mechanism for hydrogen-assisted cracking of HSS. High strength aluminum alloys pose a more complicated case, where submicron features may play an important role. We additionally discuss the following topics: (i) other cases of EAC where modified versions of the model could be applied; (ii) length scales involved in EAC.

4:15 PM Q4.5

UV-radiation induced degradation in syndiotactic polypropylene (sPP) nanocomposites. Vasilis Gregoriou, Georgia Kandilioti, Dionysios Mouzakis and Spiros Tzavalas; FORTH-ICEHT, Patras, Greece.

The influence of ultraviolet radiation on layered silicate syndiotactic polypropylene (sPP) nanocomposites was investigated in this study. The conformational and molecular alternations along with the formation of photooxidative products due to the irradiation were followed by FT-IR, X-ray diffraction and UV-visible spectroscopies. In particular, it was found that the presence of the nanoclay affects the rate of the formation of the degradation products of sPP (ketones, esters, γ -lactones, carboxylic acids etc). A significant increase in the segments characterized by helical conformation with respect to the domains with trans-planar conformation both in the nanocomposites and the neat matrix was observed by infrared spectroscopy after prolonged UV exposure. Differential scanning calorimetry (DSC) showed an increase on the overall crystallinity of sPP for all the samples after the irradiation. Additionally, UV-visible spectroscopy showed that the products created during the irradiation interacted with the polar groups of the silicate layers producing a better adhesion between the nanoclay and hydrophobic polymeric matrix. Finally, dynamic mechanical analysis (DMA) was used to examine the preservation of the mechanical integrity of these nanocomposites after UV radiation.

4:30 PM Q4.6

Epoxy-Clay Nanocomposites Subjected To Extreme Thermal Conditions and Their Effects on Materials' Permeability. Sofia Martinez Vilarino¹, David Hui¹, Leo Daniel¹ and Jianren Zhou²; ¹Composite Nanomaterials Research Laboratory, University of New Orleans, New Orleans, Louisiana; ²Mechanical Engineering, Prairie View A&M University, Prairie View, Texas.

The development of the new concept of Reusable Launch Vehicles (RLV) brings with it the necessity of finding new materials that will help to design an efficient and safe vehicle. Nanoclay-modified epoxies are being studied as candidate materials for cryogenic tanks. These new materials are studied because they have potential of improving tensile and toughening properties of the composites, in addition to the barrier properties, provided that the nanolayers of clay are well dispersed in the polymer matrix. Cryogenic tanks are subjected to extreme thermal conditions in addition to other mechanical loads. Permeation of the liquid hydrogen stored in composite fuel tanks of the RLV is one of the most critical issues on the design of the tank and the behavior of epoxy-clay nanocomposites under severe thermal stresses needs to be studied in order to determine the extent of any possible damages induced and the consequences on the permeation to

the fuel stored. The barrier properties of epoxy-clay nanocomposites are specifically studied to address cracking and permeability variations under the thermal conditions. Permeability is measured using Helium on samples of different epoxy matrices modified with 2% and 5% of two types of nanoclays, Cloisite®30B and B18, at room temperature for 12 hours with a Helium gas differential pressure of 20 psi. After the permeability coefficients are determined, these samples are subjected to severe simulated thermal cycling using a cycling machine designed and built at FAST Center, Prairie View A&M University. The samples are placed in a basket and automatically cycled between temperatures that run from -320F (-196 C) to 302F (150 C) with holding time durations of 5 minutes, respectively. After the samples are thermally cycled, examination on cracking is performed and the permeation is measured again in order to assess how the environmental conditions affect material integrity, and thus, the leakage of the tank materials. Comparison of the results before and after thermal cycling provides us some guidelines of optimization on combination of epoxy-nanoclays compositions to best withstand the harsh conditions encountered in cryogenic tanks.

4:45 PM Q4.7

Fatigue Performance and Degradation of Hydrophobic Organic Coatings. Rebecca Kirkpatrick and Christopher L. Muhlstein;

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Surface treatments are routinely used to improve the performance and appearance of structural components. When scaling down from bulk to micro, surface area plays a larger role, therefore coatings become more important. The properties of surfaces in microelectromechanical systems (MEMS) dominate the durability and performance of these structures because of their large surface-to-volume ratio. Hydrophobic organic coatings have been used in MEMS to improve yield during processing and to extend the lives of cyclically loaded surfaces in silicon components. However, recent studies suggest that the benefits of these coatings diminish under cyclic loading conditions. While the physical limitations of nanoscale, organic coatings have been observed experimentally, the underlying mechanisms of their degradation under fatigue loading conditions are unknown and cannot be extrapolated from prevailing theories for ductile, brittle, and polymeric materials. This research compares the observations of an organic coating on bulk glass to the behavior of the coating on nanoscale oxides on silicon MEMS. Bulk borosilicate glass and octadecyltrichlorosilane (OTS) were used chosen to mimic the bare and coated native oxide surfaces of a silicon MEMS. The samples were tested in dynamic fatigue, sustained load, and cyclic fatigue in order to determine 1) the ability of nanostructured, hydrophobic, organic coating to suppress stress corrosion cracking in bulk borosilicate glass and 2) if the films degrade under cyclic loading conditions. The results of the mechanical testing show that the performance of hydrophobic organic coatings may be counter intuitive. Specifically, the presence of a hydrophobic organic film on the glass surface does not guarantee enhanced resistance to environmentally-assisted cracking. Statistical analysis of the mechanical testing data shows that the OTS coating degrades the strength and environmentally-assisted cracking resistance of the glass. Moreover, this decrement does not arise due to a chemical interaction between the coating and the glass or coating procedure. Experimental data also suggests that the fatigue susceptibility of these coatings is limited to the large amplitude, cyclic strains generated in micromechanical systems, as no mechanical breakdown of the films is observed on large scale model system. Mechanistic options for the difference in behavior between bulk and micron-scale specimens will be discussed.

SESSION Q5: Degradation at Nanometer Scale:
Fundamental Processes and Mechanisms
Chairs: Prabir Patra and Vincent Rotello
Tuesday Evening, November 29, 2005
Room 209 (Hynes)

6:00 PM *Q5.1

Surface Segregation in Multicomponent Metal Oxides.

Peter A. Dowben, ¹Physics and Astronomy, University of Nebraska, Lincoln, Nebraska; ²Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska.

Surface segregation is a long standing problem in materials science. Surface segregation indicates that the surface enthalpy is different from the bulk, and occurs at finite temperatures (or in the materials growth process) when barriers to diffusion are overcome. Atomic size and lattice strain, bond strengths, and even magnetic ordering influence the extent of segregation. Rigid refractory solids are not immune from surface segregation, with surface segregation evident at temperatures that are sometimes just a very small fraction of the melting temperature (2-3%). There is now a number of

demonstrations that refractory materials are not always effective surface segregation nor surface diffusion barrier layers. Surface segregation studies were originally limited to binary alloys, but now increasingly more complex systems are under scrutiny. The study of the time and temperature evolution of the segregation is possible as a quantitative analysis of the surface composition of the ternary alloys [1-2] and multicomponent oxides [3-5] can now be obtained using angle-resolved X-ray photoemission spectroscopy, and the surface composition characterized. The detailed composition profiles in the near surface region can be then related to the free energy profile in the surface region of the stoichiometric material. Several examples of surface segregation and surface segregation driven phase separation will be discussed for illustration. Nanostructure materials are not immune from segregation, as can be shown for nanosized BaFe_{12-2x}Co_xTi_xO₁₉ barium ferrite particles. Contributions to the valence band of the nanosized BaFe_{12-2x}Co_xTi_xO₁₉ barium ferrite particles, from the cobalt and titanium dopants, can be identified and help identify segregation in these ferrite particles. Both theory and experiment provide ample demonstration that very limited dimensions of very small clusters does not necessarily impart stability against surface and grain boundary segregation. Work undertaken with N. Palina, H. Modrow (Physikalisches Institut der Universität Bonn); R. Mueller (Institut fuer Physikalische Hochtechnologie, Jena); J. Hormes, Ya.B. Losovyj (Center for Advanced Microstructures and Devices, Louisiana State University), C.N. Borca (Institute of Applied Optics, Swiss Federal Institute of Technology). The support of the NSF QSPINS MRSEC (DMR 0213808) is gratefully acknowledged. [1] D. Ristoiu, J.P. Nozières, C.N. Borca, B. Borca, P.A. Dowben, Appl. Phys. Lett. 76 (2000) 2349-2351 [2] A.N. Caruso, C.N. Borca, D. Ristoiu, J.P. Nozières, P.A. Dowben, Surface Science 525 (2003) L109-L115 [3] J. Choi, J. Zhang, S.-H. Liou, P.A. Dowben, E.W. Plummer, Phys. Rev. B 59 (1999) 13453-13459 [4] H. Dulli, E.W. Plummer, P.A. Dowben, J. Choi, S.-H. Liou, Appl. Phys. Lett. 77 (2000) 570-572 [5] C.N. Borca, B. Xu, T. Komesu, H.-K. Jeong, M.T. Liu, S.-H. Liou, and P.A. Dowben, Surf. Sci. Lett. 512 (2002) L346-L352

6:30 PM *Q5.2

Drug, Protein, and DNA Delivery with Glutathione-Mediated Release using Gold Nanoparticles. Vincent Rotello, University of Massachusetts, Amherst, Massachusetts.

Monolayer-protected gold nanoparticles provide effective vectors for the delivery of drugs and biomolecules. The ability to attach targeting functionality presents a means of delivering these carriers to target organs and tissues. Additionally, the capability of tuning surface properties provides systems that are rapidly internalized by cells, with intracellular targeting possible through the use of appropriate functionality. In addition to their ability to be functionalized in modular fashion, gold nanoparticles provide a tunable method for payload release. Glutathione (GSH) is present in low micromolar concentrations extracellularly. Intracellular GSH concentrations, however, range from 1-10 millimolar. This dramatic increase in GSH concentration within the cell provides a novel means for release: GSH can displace thiol functionality from the particle surface. This displacement process can be used directly to release drugs and prodrugs. Moreover, the addition of anionic GSH can be used to change the surface potential of cationic particles, providing an effective means for release of electrostatically-bound DNA and proteins. All of these release processes are tunable via control of the monolayer structure, with release rate correlating with monolayer length.

7:00 PM *Q5.3

Electron work function at grain boundary and the corrosion behavior of nanocrystalline metallic materials. D. Y. Li, Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

Due to their high grain boundary density, nanocrystalline materials possess unusual mechanical, physical and chemical properties. Extensive research on nanocrystalline materials has been conducted in recent years. Many studies have shown that material degradation, one of important properties of nanocrystalline materials, is crucial to their applications. In this article, the activity of electrons at nanocrystalline surfaces of several metallic materials is analyzed based the electron work function (EWF), the minimum energy required to attract electrons from inside a metal. It is demonstrated that at grain boundaries, the electron work function considerably decreases, indicating that at a grain boundary, the electron activity increases markedly. As a result, the surface becomes more electrochemically reactive. Such enhancement in electrochemical reactivity has negative effect on the corrosion resistance of nanocrystalline materials. However, for a passive metal or alloy, the nanocrystalline structure is beneficial to its corrosion resistance through rapid formation of a protective passive film. The mechanism responsible for the variation in EWF at grain boundary is discussed in this article.

7:30 PM *Q5.4

Low-Cycle Fatigue and Dynamic Fracture in Gold Thin Films on SiN Supported Membranes. Charles C. Hays, James M. Newell, Paul D. MacNeal and Warren A. Holmes; California Institute of Technology, Jet Propulsion Laboratory, Pasadena, California.

Studies of the dynamic mechanical response and fatigue behavior in Microelectro-mechanical (MEMS) systems are reported. We examined the effects of forced vibration (3-axis random vibration with 2 kHz roll-off frequency) on sub-micron thick Au-films deposited onto amorphous SiN substrates, with spider-web geometry. The resonant modes of the MEMS substrates are calculated by hand analysis and Finite Element Modeling (FEM). Scanning electron microscopy images reveal that the metallic films exhibit vibration-induced damage, with failure morphologies consistent with low-cycle fatigue, e.g., close examination of the failed regions show classic fatigue striations. In some cases, the rapid crack-growth rate of the fatigued regions resulted in localized melting of the metal film. Defect spacing was also found to correlate with resonant modes of the SiN substrate web. The origins of these observations can be traced, in part, to the large elastic limit differences between the amorphous SiN substrate, and the over-lying metal film.

SESSION Q6: Poster Session
Chairs: Ila Daryush and Orazio Puglisi
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

Q6.1

Photo-oxidation of Multiwalled Carbon Nanotubes.

B. Parekh¹, Thomas Debies², Pam Knight¹, K. S. V. Santhanam¹ and Gerald A. Takacs¹; ¹Department of Chemistry, Center for Materials Science and Engineering, RIT, Rochester, New York; ²Xerox Corporation, Webster, New York.

Multiwalled carbon nanotubes were photo-oxidized at atmospheric oxygen pressure using low-pressure Hg lamps [1] and at low pressure with emission downstream from Ar microwave plasmas [2] which are primarily atomic line sources of 253.7/184.9 nm UV and 106.7/104.8 nm vacuum UV (VUV) radiation, respectively. Surface modification was investigated as a function of treatment time with X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy and scanning electron microscopy (SEM). Results will be presented for samples treated in quartz boats and embedded in filter paper. * To whom correspondence should be addressed. Phone: 585-475-2047, Fax: 585-475-7800. E-mail address: gatsch@rit.edu [1] U. Sener, A. Entenberg, B. Kahn, F. D. Egitto, L. J. Matienzo, T. Debies and G. A. Takacs, in: Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, K. L. Mittal (Ed.), Vol. 3, 535, VSP, Utrecht (2005). [2] W. Dasilva, A. Entenberg, B. Kahn, T. Debies and G. A. Takacs, Mater. Res. Symp. Proc. 851 (Materials for Space Applications), 407 (2005); J. Adhesion Sci. Technol., 18, 1465 (2004).

Q6.2

Degradation of Polarization in Heterophase Nanostructures in the Case of Reversal of PZT-Based Relaxor Ceramics.

Galina Akbaeva¹, Viktor G. Gavriyachenko², Alexander F. Semenchev² and Igor V. Yuhnov²; ¹Institute of Physics, Rostov State University, Rostov-on-Don, Russian Federation; ²Department of Physics, Rostov State University, Rostov-on-Don, Russian Federation.

Relaxor ferroelectrics are considered as a set of nanodimensional polar and nonpolar regions the ratio of which in the bulk of ceramics is temperature-dependent. In the process of cooling the polar regions expand and the domain structure of a ferroelectric phase is formed from nanodomains formed in the initial polar regions. Thus, a relaxor ferroelectric is a heterogeneous system containing a large number of domain walls as well as interphases. This fact defines a process of reversal of polarization and its degradation under the long action a strong sign-alternating electric field. The electrical dynamic fatigue in the process of repeated reversal of polarization of the samples prepared by the hot-pressing method from the PZT-based material modified with germanium was studied by experiments. This material shows the properties of ferrosoft relaxor ceramics [1-3]. It has been established that the decrease of the remanent polarization magnitude after 1 000 000 cycles of the polarization reversal for the samples containing 1 % of germanium oxide is about 40 %, and the coercive field increases by 15 % in this case. For the samples containing 2 % of the additive the polarization degradation process is not so pronounced: the decrease of the remanent polarization does not exceed 10 % after 10 000 000 cycles of the polarization reversal. The

coercive field for such samples monotonously decreases by 10 % of the initial value with the increase of the number of cycles of the polarization reversal. The complex studies of dielectric, electromechanical and structural characteristics of the samples enabled us to make suggestions about the process of polarization degradation during the reversal of the relaxor ferroelectric. References [1] G.M. Akbaeva, A.Ya. Dantsiger, and O.N. Razumovskaya, Proc. Intern. Conf. Electroceramics IV, Aachen, Germany, 1994, v.1 (Aachen, 1994), p.535. [2] A.V. Shilnikov, I.V. Otsarev, A.I. Burkhanov, V.N. Nesterov, and G.M. Akbaeva, Ferroelectrics, v.222, p.311 (1999). [3] G.M. Akbaeva, A.V. Shilnikov, A.I. Burkhanov, and Yu.N. Mamakov, Integr. Ferroelectrics, v.39, p.137 (2001).

Q6.3

Investigations of DC Electrical Resistivity in Electron-Beam Modified Carbon Nanotube Films. Sanju Gupta, N. D. Smith and R. J. Patel; Physics and Materials Science, Missouri State University, Springfield, Missouri.

Carbon nanotubes in the family of nanostructured carbon materials are of great interest because of several unique physical properties. For space applications, it needs to be shown that CNTs are physically stable and structurally unaltered when subjected to irradiation is indispensable. The carbon nanotube films were grown by microwave CVD technique using Fe as catalyst and by varying the thickness of the Fe layer, synthesis of both single- and multiwalled nanotubes were achieved. To conduct such study, they were subjected to low and medium energy electron-beam irradiation [50 keV; flux of 10^{22} electrons/cm²·s] continuously for a few to several hours to study their influence on structure and the corresponding electrical properties to establish property-structure correlations [1]. Microstructural and physical properties characterizations are made prior to and post-irradiation include scanning electron microscopy (SEM), Raman spectroscopy (RS), high-resolution transmission electron microscopy (HRTEM), and current versus voltage (I-V) measuring resistivity. Experimental studies show multi-walled nanotubes tend to be relatively more robust than those of single-walled. This is because increased exposure on an occasionally found individual bundle of single-wall nanotubes tended to graphitize, pinch, and crosslink similar to polymers forming intra-molecular junction (IMJ) within the area of electron beam focus, which is possibly through aggregates of amorphous carbon [1], revealed through SEM and TEM. It is also suggestive that knock-on collision may not be the primary cause of structural degradation, rather but a local gradual reorganization occurs. Dramatic improvement in the I-V properties for single-walled (from semiconducting to quasi-metallic) and relatively small but systematic behavior for multi-walled (from metallic to more metallic) with increasing irradiation hours is discussed in terms of critical role of defects. Alternatively, contact resistance decreases by orders of magnitude when exposed to the electron beam in SEM. For all measurements, resistance values lie in a range of 3 - 10 kilo-ohms at room temperature. The results also indicate that multi-walled nanotubes tend to reach a state of damage saturation, suggesting the possibility of development of radiation shields for short-term space missions. More importantly, they provided a contrasting comparison between semiconducting (single-wall) and metallic (multiwall) nanotubes i.e. diameter dependence. This work is supported by CASE and SGs internal funds. [1] S. Gupta, R. J. Patel, N. D. Smith, Mater. Res. Soc. Symp. Proc. 851, NN6.3-NN6.10 (2004); S. Gupta, R. J. Patel, N. D. Smith, Y. Y. Wang, R. E. Giedd, J. Appl. Phys. (2005) (submitted).

Q6.4

Degradation of Assembled Silicon Nanostructured Thin Films: a Theoretical and Experimental Study. Valeria Bertani, Luisa D'Urso, Alessandro Alfio Scalisi, Giuseppe Compagnini and Orazio Puglisi; Dept of Chemistry, Catania University, Catania, Italy.

The study of the structures and properties of small elemental clusters has been an extremely active area of current research, due to the peculiar behavior of these species halfway between that of single atoms and of the bulk phase. In this work silicon nanoclusters are generated by ablation of a high purity polycrystalline rod with a pulsed laser vaporization source and then deposited on a support. Their structure is studied both in the gas phase by means of Time of Flight Mass Spectrometry and in the solid phase through in situ Raman and Infrared Spectroscopy. The spectra reveal that the as deposited clusters are hydrogenated with negligible amount of oxide. Degradation of silicon nanoclusters has been studied after gas exposure. In the gas of air a consistent modification was observed, leading to a near-infrared luminescent silicon nanoparticles. In the second part of the work density functional theory is applied to investigate the geometrical structure of silicon clusters and their interaction, in term of structure and energy, with different gases. The calculations were performed with the Gaussian 03 program suite, adopting the B3LYP functional to calculate the exchange and correlation energy. Si8 has been chosen as model cluster to study the

degradation of silicon clusters both kinetically and thermodynamically, in order to explain the experimental evidences. Experimental and calculated infrared spectra are compared.

Q6.5

Ion desorption by inner-shell excitation and photodegradation of poly(vinylidene fluoride). Koji Okudaira¹, Eiichi Kobayashi², Satoshi Kera¹, Kazuhiko Mase² and Nobuo Ueno¹; ¹Faculty of Engineering, Chiba University, Chiba, Japan; ²Institute of Materials Structure Science, Tsukuba, Ibaraki, Japan.

Recently, much interests related to ferroelectric polymer have been concentrated for the application of an infrared sensor, ultrasonic transducer, and nonvolatile memory. Vinylidene fluoride and trifluoroethylene copolymer is a well-known ferroelectric material. However, a manufacturing of the fluorinated polymer such as poly(vinylidene fluoride) (PVDF) was difficult since there are few solvents to dissolve these polymers. Recently we reported that PVDF shows an effective F⁺ ion desorption followed by C-F bond scission by the irradiation of photon corresponding to the transition from F 1s to $\sigma(\text{C-F})^*$. Ion desorption induced by core-level excitations is one of the active fields in the surface science. The analysis of desorption ion by inner-shell excitation is one of useful methods for clarification of the relationship between the photodegradation mechanism and the electronic configuration of excited states. For photo-stimulated ion desorption, an Auger-stimulated ion desorption (ASID) mechanism has been proposed. The Auger-electron photo-ion coincidence (AEPICO) method has become one of the most powerful tool because it can be used to measure ion desorption yields for a selected core excitation or a selected subsequent Auger. Experiments were performed at the beamlines BL8A and 13C at the Photon Factory of the High Energy Accelerator Research Organization. AEPICO spectra were measured by using the EICO apparatus, which is composed of a coaxially symmetric mirror electron energy analyzer and a compact time-of-flight ion mass spectrometer. Total ion yield (TIY) and total electron yield (TEY) spectra of PVDF film near fluorine (F) K-edge region were observed. In the TIY/TEY, an intense peak at $h\nu=690.5$ eV, (corresponding to the transition from F1s to $\sigma(\text{C-F})^*$), indicates that effective F⁺ desorption occurs. From the photon energy dependence of Auger electron spectra (AES) at F 1s region, it is found that at $h\nu=690.5$ eV, an intense Auger peak appears at $E_k=650$ eV. At $h\nu=740$ eV (above F1s ionization energy, where the normal-Auger process occurs mainly), the intense Auger peak does not present at $E_k=650$ eV. Since the spectator-Auger transition is reported to be minor processes, the spectator-Auger electron mainly contributes the intense Auger peak. AEPICO for F⁺ at $h\nu=690.5$ eV gives a large intensity at $E_k=650$ eV. E_k position of this intense AEPICO peak agrees with that of the Auger spectra, indicating that the most probable mechanism is that F⁺ ion desorption induced by the transition from F 1s to $\sigma(\text{C-F})^*$ is a spectator-Auger stimulated ion desorption process.

Q6.6

Proton Radiation Damage in CdSe/ZnS Nanocrystals. Sriram Dixit¹, Dmitry Koktysh², Sandra J. Rosenthal^{2,1} and Leonard C. Feldman^{3,1}; ¹Interdisciplinary Materials Science, Vanderbilt University, Nashville, Tennessee; ²Department of Chemistry, Vanderbilt University, Nashville, Tennessee; ³Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee.

Radiation tolerance in nanocrystalline materials may be significantly different from the bulk due to the large surface contributions and quantum-size effects. One of the most ideal nanocrystalline materials is CdSe quantum dots containing excellent size distributions and optical properties. We have measured the proton irradiation effects on the optical properties of CdSe/ZnS core-shell nanocrystals. Films of these colloidal nanocrystal core-shells with sizes of 3-6 nm, were prepared by spin casting onto a graphite substrate and exposed to protons at energy of 1.8 MeV with flux varying from 3.125×10^{14} cm⁻² to 3.125×10^{15} cm⁻² and an average current of 40 nA. Defect levels introduced below the conduction band due to this irradiation allow for non-radiative recombination, thereby decreasing the luminescence after proton beam damage. The change in the absorption and photoluminescence of these nanoparticulate films was monitored as a function of the hydrogen dose. With an increase in the irradiation dosage, the photoluminescence is quenched with a cross-section for damage of 2.15×10^{-16} cm²/nanocrystal for a 3 nm size nanocrystal. Interestingly the luminescence of the CdSe/ZnS nanocrystals due to the proton beam, as well as the reduction of this luminescence with beam damage, could be observed directly. Finally the results for the nanocrystals are compared to similar results of bulk CdSe.

Q6.7

Transport Properties of Single-walled Carbon Nanotubes under Pressure. Jie Tang^{1,2}, Taizo Sasaki¹ and Lu-Chang Qin²;

¹National Institute for Materials Science, Tsukuba, Japan; ²University

of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

A carbon nanotube can be electronically either a semiconductor or a metal, depending on its diameter and helicity, and the electronic band structure is sensitive to the cross-sectional geometry of the concerned nanotubes. Single-walled carbon nanotubes are compressed easily under hydrostatic pressure with a high volume compressibility of 0.024/GPa[1]. The single-walled carbon nanotubes are polygonized when they form bundles of hexagonal close-packed structure and the inter-tubular gap is smaller than the equilibrium spacing of graphite. When the pressure increases, further polygonization occurs to accommodate the extra amount of volume reduction. Accompanying polygonization, a discontinuous change in electrical resistivity was observed at 1.5 GPa pressure, suggesting that a phase transition had taken place. From the relationship between electrical resistivity and temperature, the nanotube material showed a semiconducting behavior. When the pressure is below 1.5 GPa, the band gap exhibited a monotonic increase with increasing pressure. This phenomenon is attributed to the fact that, as the pressure increased, the band gap of the semiconducting nanotubes increases as a result of polygonization. However, at 1.5 GPa pressure, a structural phase transition is suggested to have occurred in which the polygonized nanotubes become elliptical in cross-section which also led to the sudden drop in band gap. [1] J. Tang, L.-C., Qin, T., Sasaki, M., Yudasaka, A., Matsushita and S. Iijima, Phys. Rev. Lett. 85,1887 (2000).

Q6.8

Degradation Phenomenon in Semiconductive Nanoamorphous Structures from Molybdenum Oxide. Armen Markosyan and Razmik Malkhasyan; Scientific production enterprise "ATOM", Yerevan, Armenia.

The condition of degradation of electrical properties of nanoamorphous metals and their semiconductive oxides in the course of time is discovered and studied when investigating electro-physical properties of the given materials for the first time synthesized at Scientific Production Enterprise ATOM. The resistance of ware in the open air changes over a period of several years. However it decreases and is comparatively fast stabilized when placed in vacuum. Thermal training in vacuum at temperature up to 80-100 oC, within 3-6 hours leads to the stabilization of studied semiconductive nanoamorphous ware. The optimal conditions of thermal stabilization are studied. Relaxation and stabilization in studied systems are accompanied by irreversible decrease of resistance as a whole for several times. The given phenomenon has common nature and concerns all wares obtained from pressed nanosize powders and is especially important for amorphous nanosize metals and compounds on their basis. It is shown that degradation effect in ware from nanostructured (amorphous and crystalline) materials in the main is defined by magnitude and the condition of their pores.

Q6.9

Stability of Size Selected Silver Nanoparticles in Water. Yuko Shimizu, Masahiro Watanabe, Hiroshi Yao and Keisaku Kimura; Graduate School of Material Science, University of Hyogo, Hyogo, Japan.

Production of nano-meter sized silver is a current interest due to peculiar electronic and optical properties induced by quantum size effect. These properties are expected to play a key role in the coming nano-technology devices. Different from gold nanoparticles in which there are coexistence of plasmon band and inter-band transition, silver nanoparticles has unique plasmon band in the visible region. Hence a precise size separation with massive production is eagerly waiting. Size fractionation of cluster-sized materials is possible by using the state-of-the-art technique as in gold cluster materials by PAGE (polyacrylamide gel electrophoresis) method (R.L.Wetten et al, JPC,102 (1998)10643, Y.Negishi et al, JACS,126 (2004)6518). However, it is not yet known whether it is capable of separating nanoparticles by this technique to what extent in size or not at all. Surface modified silver nanoparticle was prepared by reduction of silver nitrate by NaBH₄ in the presence of di-carboxylic thiols, mercaptosuccinic acid, under anaerobic and dark conditions followed by condensation, separation and washing processes to remove unbound starting substances and reaction by-products. The purity of the starting materials was evidenced by crystallization of these particles into superlattices, the size of this particle crystals reaches to 0.1 micron-meter, as reported elsewhere. The magic numbered silver particles once extracted by PAGE technique. It was found that these fractions were unstable to decompose to lower sized substances as clarified by their color changes. In the past, the stability of size-selected metallic clusters has been studied and discussed in the context of free clusters with magic number and seldom discussed in supported clusters or nanoparticles. Here we will report the separation details and observation of its stability as functions of temperature, absence or existence of light illumination and supporting gel constituents. All our observation has questioned that the stability of

magic numbered substances is absolute? It seems that it strongly depends on the circumstance of the particles in the suspension conditions.

Q6.10

Sintering of HAp Precipitated from Solutions Containing Ammonium Nitrate and PVA. Tatiana V. Safronova¹, Valery I. Putlyayev¹, Alexey V. Belyakov² and Mikhail A. Shekhirev¹; ¹Chemistry, MSU, Moscow, Russian Federation; ²Department of Chemical Technology of Silicates, MUCTR, Moscow, Russian Federation.

Bioceramics based on hydroxyapatite (HAp) is known to be a prospective material for biomedical applications. However, sintering of HAp is still understudied in sense of reasonable selection of controlling parameters. In particular, the role of impurities and co-products of powder fabrication is still questionable. The data concerning the role of ammonium nitrate coming to precipitated HAp from the mother liquor, its effect on powder compaction and subsequent sintering, are not available. Nanosized powders of HAp were fabricated via conventional wet-precipitation technique by dropwise adding of Ca(NO₃)₂ solution (0.25 -1.67 M) to the stock solution of (NH₄)₂HPO₄ (0.15-1.00 M) with pre-adjusted pH at 60 °C in presence of polyvinyl alcohol (PVA). PVA was added to the stock solution in order (i) to block crystal growth during synthesis, (ii) to improve stability of HAp suspension to sedimentation, (iii) to reduce an aggregation of HA nanoparticles in the stage of drying. NH₄NO₃ - a co-product of the precipitation reaction, presented in as-precipitated powder in amount of 30%, was evaluated as an additive affecting a compaction of the powder and the initial stage of a sintering. The powder samples were tested by XRD, FTIR, light-scattering, TEM and SEM/EDX to get particle sizes, morphology and chemical composition, dilatometry. Ceramics were sintered at 700-1250 °C and evaluated with SEM/EDX and density measurements. Addition of PVA to the stock solution in the course of HAp precipitation is a promising technique to control an aggregation of HAp nanoparticles in the stages of drying and sintering. PVA acting as a surfactant in the solution and as a binder in dry powder can keep highly reactive small HAp particles within large agglomerates providing better molding of the powder and controllable densification of ceramics. The effect of PVA on microstructure of the HAp powder and their sintering behaviour is discussed in terms of self-organisation concept and synergetics.

Q6.11

Thermal degradation of poly(vinyl-N-pyrrolidone)/Ag and Au nanoparticle composites. Lauren Rast, Sarah Schaefer, Heather Williamson and Andrei Stanishevsky; University of Alabama at Birmingham, Birmingham, Alabama.

Polymers often serve as a component of the reaction medium for metal nanoparticle synthesis and as protective layers to avoid nanoparticle aggregation. The polymer matrix has to be removed either chemically or thermally for some nanoparticle applications. At the same time, polymer/metal nanoparticle composites attract great attention due to the interesting optical properties of these systems. The nature of interaction between the matrix and nanoparticles affects the stability of the composite, especially at elevated temperatures. In this work, we investigated the effect of thermal processing on the degradation of polyvinyl-N-pyrrolidone (PVP)/Ag and PVP/Au nanoparticle composites. Silver and gold nanoparticles with a particle size in the range from 7 to 20 nm were prepared by the reduction reaction of AgNO₃ and HAuCl₄, respectively, in the presence of PVP. The mass ratio of PVP to metal salt was varied from 0.2:1 to 10:1. The samples of the composite PVP/nanoparticle material were dip- or spin-coated onto silica substrates. The structure, composition, and optical properties of the composites were studied in the temperature range from 25 °C to 550 °C using thermogravimetry analysis, FT-IR, Raman, and UV-Vis spectroscopies, and X-ray diffraction. We found that the interaction between the PVP molecule and metal induces the local decomposition of the polymer at relatively low temperature (around 180 °C) causing the PVP cross-linking and changes in optical properties. However, the nanoparticle size does not change up to 400 °C depending, in part, on the PVP/metal nanoparticle ratio. Silver nanoparticles showed stronger effect than gold on the decomposition of PVP. We discuss the possible mechanisms of decomposition of the PVP/metal nanoparticle composite.

Q6.12

Thermal stability of CNT-Al₂O₃ nanocomposite fabricated by thermal CVD. Seokjun Hong, Jaewoong Choi, Junhye Song, Gilho Hwang, Yongho Choa and Sungoon Kang; Hanyang University, Seoul, South Korea.

These days many researchers have studied about CNT-ceramic nanocomposite which has good electrical and mechanical properties. However, the agglomeration, which is the specific property of CNT,

makes the homogeneous dispersion of CNT and matrix difficult. Thus, we devised the new process to make the homogeneous dispersion of CNT and matrix via aluminum oxide powder. Fe precursor was formed on the surface of the aluminum oxide powder and Al₂O₃ based CNT powders were obtained by the thermal CVD with C₂H₂ reactive gas. The particle size of CNT-Al₂O₃ powder was about 25-43 nm and the homogenous dispersion accomplished. The bulky CNT-Al₂O₃ nanocomposite was fabricated by SPS (Spark Plasma Sintering) at 1300 °C. The thermal stability of CNT-Al₂O₃ nanocomposite was analyzed by TG-DSC, XRD, TEM, and SEM.

SESSION Q7: Magnetic Nanocomposites
Chairs: Tamio Endo and Ralph Skomski
Wednesday Morning, November 30, 2005
Room 209 (Hynes)

8:00 AM *Q7.1

Magnetic Properties and Microstructure of Fe-Cu Composites. W. Kappel, Materials, National Institute for R&D for Electrical Engineering ICPE-Advanced Research, Bucharest, Romania.

New magnetic composite materials, obtained by melt-spinning, with the nominal composition Fe_xCu_{100-x} (where x = 20; 50; 80) were characterized by XRD analysis, SEM and magnetic measurements. The structural aspects, like phase composition, size and texture effects, have been corroborated with the magnetic properties. Also some addition of B or Ni were studied. Finally, the possibility to choose the adequate chemical composition and the suitable processing route, in order to obtain the desired anisotropic magnetic materials, were presented.

8:30 AM *Q7.2

Magnetization Reversal Processes in Exchange-Biased MnPd/Co Films. Dominique Givord¹, Cristina Macovei¹, Nguyen N. Phuoc² and Nguyen P. Thuy²; ¹Laboratoire Louis Neel, CNRS, Grenoble, France; ²ITIMS, Hanoi University of Technology, Hanoi, Viet Nam.

Magnetic bilayers were prepared, associating a Mn_xPd_{1-x} (x = 0.2) antiferromagnetic (AFM) layer, with thickness 3 nm < t_{MnPd} < 12 nm and a ferromagnetic (FM) Co layer, with thickness t_{Co} = 18 nm. Exchange-bias was found in samples cooled from a temperature above 150 K, in a magnetic field of the order of 0.4 T. In all samples, the first magnetization reversal is very abrupt whereas magnetization reversal measured on the following cycles is more progressive. At low temperatures, the thermal variations of the coercive field, H_c, and that of the exchange-bias field, H_{EB}, deduced from measurements on the symmetrical hysteresis cycles are similar; the exchange-bias fields vanishes at about 150 K, whereas a weak coercive field persists at higher temperature. We will focus more particularly on the analysis of the magnetization reversal processes in these systems. Except during first reversal, magnetization reversal reveals that a large distribution of energy barriers is present. Under such conditions, reversal may be described within an approach which is classically applied to the analysis of hard magnet reversal processes. Comparing the time dependence of the magnetization to the irreversible susceptibility gives access to the so-called activation volume, v_{act}, within which reversal is initiated. Simultaneously, a very significant reversible contribution is found to contribute to the magnetic susceptibility. The small value of v_{act} in the exchange-biased systems and the large value of the irreversible susceptibility are tentatively related to the highly frustrated magnetic configuration which is expected to exist at the FM-AFM interface. This is in agreement with numerical modelling. The specificity of the first reversal process with respect to the processes observed during the following cycles will be associated to the fact that interface moment disorder is much weaker in the virgin state than after any magnetization processes has occurred. This is consistent with the observation that first reversal is dominated by the formation of a small number of nuclei, which may be assumed to be all identical. Consistently, the time dependence of the magnetization at a given temperature is given by b(t) = exp(-Rt) where b(t) = (M(t) + M_s) / 2M_s (M(t) magnetization at time, t, M_s, spontaneous magnetization). The low-temperature magnetic domain configurations, in the virgin state and after reversal has occurred, will be analyzed on the basis of Kerr effect magneto-optical observations. Finally, the differences between the first and following reversal processes will be discussed in the framework of the so-called disorder-induced criticality [1], as already proposed for the Co/CoO system [2]. [1] A. Travesset, R. A. White, and K. A. Dahmen, Phys. Rev. B66, 024430 (2002) [2] A. Berger, A. Inomata, J. S. Jiang, J. E. Pearson, and S. D. Bader, Phys. Rev. Lett. 85, 4176 (2000)

9:00 AM *Q7.3

Suppressed Magnetization in La_{0.7}Ca_{0.3}MnO₃/YBa₂Cu₃O_{7-δ}

Superlattices. Suzanne G. E. te Velthuis¹, A. Hoffmann¹, Z. Sefrioui², J. Santamaria², M. R. Fitzsimmons³, S. Park³ and M. Varela⁴; ¹Argonne National Laboratory, Argonne, Illinois; ²Universidad Complutense de Madrid, Madrid, Spain; ³Los Alamos National Laboratory, Los Alamos, New Mexico; ⁴Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The interplay between ferromagnetism and superconductivity has been of longstanding research interest, since the competition between these generally mutually exclusive types of long-range order gives rise to a rich variety of phenomena. In particular, layered systems enable a straight-forward combination of the two types of long-range order. There is interest in studying these effects in superlattices of high Tc superconductors and colossal magnetoresistance oxides, where the superconducting and ferromagnetic properties are depend strongly on the charge carrier density and thus charge transfer across the interface may be important. In a series of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superlattices, SQUID magnetometry showed that the LCMO saturation magnetization is significantly reduced. Polarized neutron reflectometry determined that the reduced moment is due to an inhomogenous magnetization profile. Specifically, the magnetization in each LCMO layer is suppressed close to the interfaces with the YBCO, possibly due to charge transfer across the interface. Work supported by MCYT MAT 2002-2642, CAM GR- MAT-0771/2004, UCM PR3/04-12399 and by the U.S. Department of Energy, Basic Energy Sciences under contracts W-31-109-ENG-38, W-7405-ENG-36, and DE-AC05-00OR22725.

9:30 AM *Q7.4

Growth Mechanisms and Oxidation-Resistance of Gold-Coated Iron Nanoparticles. Kai Liu, University of California, Davis, California.

Core/shell structured nanoparticles, due to the close proximity of the two functionally-different components, could exhibit enhanced properties and new functionality. They are ideal for exploring proximity effects, structure stabilization, and functionalization. Core/shell structured magnetic nanoparticles have potential applications in remote magnetic manipulation, magnetic resonance imaging, cell tagging and sorting, and targeted drug delivery. Here we report the synthesis of Fe-core/Au-shell nanoparticles by a reverse micelle method, and the investigation of their growth mechanisms and oxidation-resistant characteristics.^{1,2} The core-shell structure and the presence of the Fe & Au phases have been confirmed by transmission electron microscopy, energy dispersive spectroscopy, X-ray diffraction, Mössbauer spectroscopy, and inductively coupled plasma techniques. Additionally, atomic-resolution Z-contrast imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) have been used to study details of the growth processes. The Au-shell grows by nucleating on the Fe-core surface before coalescing. Magnetic properties and their variations due to oxidation have been studied by SQUID, vibrating sample magnetometry, and a first order reversal curve (FORC) method.^{3,4} The magnetic moments of such nanoparticles, in the loose powder form, decrease over time due to oxidation. The less than ideal oxidation-resistance of the Au shell may have been caused by the rough Au surfaces. However, in the pressed pellet form, electrical transport measurements show that the particles are fairly stable, as the resistance of the pellet does not change appreciably over time. Work done in collaboration with Sung-Jin Cho, Juan-Carlos Idrobo, Justin Olamit, J. E. Davies, Nigel D. Browning, Susan M. Kauzlarich, Fernande Grandjean, Leila Rebbouh, and Gary J. Long, supported by NSF, ACS-PRF, DOE, UC-CLE, Ministère de la Région Wallonne and UCD-NEAT-IGERT. [1]. S. Cho, S. M. Kauzlarich, J. Olamit, Kai Liu, F. Grandjean, L. Rebbouh, and G. J. Long, J. Appl. Phys. 95, 6804 (2004). [2]. S. Cho, J. C. Idrobo, J. Olamit, Kai Liu, N. D. Browning, and S. M. Kauzlarich, Chem. Mater., 17, 3181 (2005). [3]. J. E. Davies, O. Hellwig, E. E. Fullerton, G. Denbeaux, J. B. Kortright and Kai Liu, Phys. Rev. B 70, 224434 (2004). [4]. J. E. Davies, O. Hellwig, E. E. Fullerton, J. S. Jiang, S. D. Bader, G. T. Zimanyi, and Kai Liu, Appl. Phys. Lett. 87 (1) (2005); cond-mat/0504492.

10:30 AM *Q7.5

Effects of ion-beam irradiation on the L1_0 phase transformation and their magnetic properties of FePt and PtMn films. Chih-Huang Lai¹, Sheng-Huang Huang¹, C. C.

Chiang¹, S. H. Liou², D. J. Sellmyer², M. L. Yan², L. Yuan² and T. Yokata³; ¹Materials Science and Engineering, National Tsing Hu University, HsinChu, Taiwan; ²Physics, University of Nebraska, Lincoln, Nebraska; ³Environmental Engineering of Materials, Nagoya Institute of Technology, Nagoya, Japan.

Ion-beam irradiation shows degradation or enhancement of magnetic properties on L1_0 phase of FePt and PtMn films. A highly ordered L1_0 FePt phase was directly achieved by using 2 MeV He-ion irradiation without conventional postannealing. The in-plane coercivity greater than 5700 Oe can be obtained after disordered FePt films were

irradiated at the beam current of several $\mu\text{A}/\text{cm}^2$ with the ion dose of 2.4×10^{16} ions/ cm^2 . The high beam-current-density results in direct beam heating on samples. In addition, the irradiation-induced heating process provides efficient microscopic energy transfer and creates excess point defects, which significantly enhances the diffusion and promotes the formation of the ordered phase. Consequently, the direct ordering of FePt took place by using ion-irradiation heating at temperature as low as 230 C. Due to the fast temperature rise, this ion-irradiation heating treatment can be used as an alternative technique for the rapid thermal annealing (RTA). The comparison has been made on the [Fe/Pt] $_{10}$ /C films by RTA and high current-density He irradiation. The sample prepared by RTA at 550 C has (001) texture and strong magnetic perpendicular anisotropy with Hc of 6 KOe. The sample irradiated at 5.04 $\mu\text{A}/\text{cm}^2$ has Hc of 10 KOe but has isotropic magnetic properties due to the (111) texture. Although RTA and ion irradiation both reach similar temperature, ion irradiation seems to suppress the (001) texture leading to isotropic Hc. Ion-beam irradiation can also be applied to the transformation of PtMn. An ordered PtMn phase and a large exchange field of 1000 Oe were obtained in CoFe/PtMn bilayers by using 1.25 $\mu\text{A}/\text{cm}^2$ He ions at presence of a magnetic field of 650 Oe during irradiation. On the other hand, O ion irradiation totally destroyed the exchange field. Due to the feasibilities of the focused beam size, the ion-irradiation can be potentially used for the magnetic patterning.

11:00 AM *Q7.6

Magnetic Nanocomposites Assembled by Monodisperse Nanoclusters as Building Blocks. You Qiang¹, Jiji Antony¹, Amit Sharma¹, Joseph Nutting¹, Daniel Meyer¹ and Zachary Billey²; ¹Physics, University of Idaho, Moscow, Idaho; ²Department of Physics, Linfield College, McMinnville, Oregon.

Recently, there is a great attention on magnetic thin films and nanocomposite assembled by nanoclusters as building blocks. The development on new advanced nanocomposites that possess unique magnetic and optical properties with sustainability in different harsh space environments will be a future challenge in materials science and engineering industry. We have developed a new cluster deposition system, which combines a kind of sputtering-gas-aggregation (SGA) cluster beam source with two atom beams from standard magnetron sputtering. This system is used to deposit simultaneously or alternately magnetic thin films or multilayers, and offers the great ability to control independently the incident cluster size and density, and thereby the interaction between clusters and cluster-matrix material which is of interest for fundamental research and industry applications. We have studied the mechanism of cluster formation, size distribution and morphology of thin films deposited by using a low-, medium- and high-energy cluster beam. Two examples of soft nanocomposites made out of Fe or Co nanoclusters, and ferromagnetic semiconductor films of doped ZnO nanoclusters show this new technology allows unprecedented flexibility in the creation of new types of nanostructured thin films. Nanocluster size, shapes and nanocrystalline structures have been studied by TOF, AFM, XRD, XPS, TEM and HRTEM. Magnetic and optical properties of those films have been investigated by SQUID, MFM and UV-photoluminescence. An interesting dependence of magnetization was found on the cluster size and the concentration in a matrix. Both significant ferromagnetism and large UV-blueshift at room temperature appear in same cluster films, which are highly important for space applications of spintronic devices. * Research supported by NSF-EPSCoR, Battelle and DOE-EPSCoR.

11:30 AM Q7.7

Magnetic Aging. R. Skomski, J. Zhou and D. J. Sellmyer; Department of Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska.

Magnetic properties such as the remanent magnetization exhibit a slow temperature dependence. Depending on the context, this degradation is known as magnetic aging or magnetic viscosity. For example, permanent magnets lose a fraction of their remanence each decade. Our presentation focuses on the fundamental physics of the aspect. Initially, it was thought to be related to mechanisms such as eddy currents, but soon it became clear that this is merely a secondary consideration. There are two types of magnetic aging, namely structural aging and thermally activated magnetization processes. Structural aging refers to both the crystal structure and to defects. Time-dependent structural changes are important, for example, in metastable intermetallics such as $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ permanent magnets, where the decay into SmN and Fe equilibrium phases limits the maximum application temperature. A mechanism involving both structural and magnetic degrees of freedom is the Snoek aftereffect. It occurs in steels and related materials and means that magnetic domain walls interact with diffusing carbon atoms. Thermally activated magnetization reversal is of great importance in areas such as permanent magnetism and magnetic recording. Their dynamics is

approximated by the Kramers-Arrhenius or Néel-Brown law, where the relaxation time is proportional to $\exp(-E/kT)$. The magnetization is then obtained by analyzing the field-dependent activation energy $E(H)$ for realistic energy landscapes. However, the applicability of the exponential Arrhenius-Néel law is limited to energy barriers much higher than the thermal energy kT . In the small-particle or superparamagnetic limit, this is not necessarily satisfied. Generalizations of the exponential law are obtained from the magnetic Fokker-Planck equation. Ignoring the deterministic precession of the spin, the magnetization decay has the character of diffusion in spin space, and the resulting time dependence is more complicated than an exponential law. Exact and approximate solutions will be presented for one and three-dimensional systems, respectively. This research is supported by the W. M. Keck Foundation, NSF-MRSEC, INSIC, and CMRA.

11:45 AM Q7.8

Long-Term Information Loss in Magnetic Recording Media. J. Zhou, R. Skomski and D. J. Sellmyer; Department of Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska.

Magnetic recording has been a driving force in nanotechnology and electronics. The key advantage is the high storage density, corresponding to bit sizes much smaller than the wavelength of visible light, but a fundamental bit-size limit is given by the thermal stability of the stored information [1]. In very small grains or particles, thermal activation leads to local magnetization reversal and to the decay of the stored information. In the Stoner-Wohlfarth model, the zero-field energy barrier is KV , where K and V are the anisotropy and the volume of the particle, respectively. In the simplest limit, the magnetization decay is exponential, described by an Arrhenius-type exponential law $\exp(-KV/kT)$. The Stoner-Wohlfarth model lumps the real structure of the medium into the quantities K and V , which acquire the character of difficult-to-interpret parameters. However, after appropriate renormalization, the time dependence of the magnetization is surprisingly well described by power laws reminiscent of the original Stoner-Wohlfarth theory [2]. Our presentation deals with two aspects of this renormalization: (i) the derivation of effective parameters K and V for a given geometry and (ii) fundamental limit to the exponential law $\exp(-KV/kT)$. One explicitly considered case is an elongated particle of diameter D and length L . Since $V \propto L$, elongation helps to increase KV , but there is no additional gain in thermal stability when L is much larger than the domain-wall width. We present the activation energies for typical nonlinear modes and analyze the temperature dependence of the corresponding magnetization decay. The applicability of the exponential law is limited by local thermodynamic fluctuations. In the Stoner-Wohlfarth model, as well as in more sophisticated model calculations and simulations, K is assumed to be a materials constant. However, this approach ignores various factors, including time-dependent local anisotropy fluctuations. The local fluctuations are most pronounced in small grains or particles and negatively affect the thermal stability. This is important in two-phase systems, where a soft-magnetic phase improves the writability by reducing the coercivity but is likely to reduce the energy barrier. Thermal fluctuations in the soft phase translate into a random exchange field acting on the hard phase and reduce the energy barrier. Simplifying somewhat, a conclusion is that additional ferro- or antiferromagnetic phases may improve figures of merit such as coercivity but are harmful to the storage density. This research is supported by the W. M. Keck Foundation, NSF-MRSEC, INSIC, and CMRA. [1] D. Weller and A. Moser "Thermal effect limits in ultrahigh density magnetic recording", IEEE Trans. Magn. **35**, 4423-4439 (1999). [2] R. Skomski, "Nanomagnetics", J. Phys.: Condens. Matter **15**, R841-896 (2003).

SESSION Q8: Miscellaneous Processes and Mechanisms
at Nanometer Scale
Chairs: Sanju Gupta and You Qiang
Wednesday Afternoon, November 30, 2005
Room 209 (Hynes)

1:30 PM Q8.1

Size Control and Spectroscopic Characterization of Monolayer Protected Gold Nanoparticles Obtained by Laser Ablation in Liquids. Giuseppe Compagnini, Orazio Puglisi and Alessandro A. Scalisi; Dipartimento di Scienze Chimiche, University of Catania, Catania, Italy.

Formation of metal nanoparticles by laser ablation of solids in liquid environment has attracted much attention in the last few years. It is an alternative way to well known chemical routes, and it is characterized by the absence of any counter-ion contamination or surface active substances. In this work, we present a study on the formation of gold colloids by laser ablation of a gold metal target in

alkanes and thiol-alkane solutions. Gold particles are found to be coated with an alkyl shell, thus obtaining Monolayer Protected Metal Nanoparticles. The role of thiol molecules is to avoid the degradation of the sol, preventing agglomeration and controlling the particle size. Results show a decrease of the gold particle size down to 1.5 nm by increasing the thiol concentration. The electronic structure of gold core and the vibrational properties of the capping hydrocarbon chains reveal effects connected with the nanosized nature of the particles.

1:45 PM Q8.2

Modeling of Coarsening Processes in Patterned Systems.

Mark Jhon^{1,2}, Andreas M. Glaeser^{1,2} and Daryl C. Chrzan^{1,2};

¹Materials Science and Engineering, University of California at Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratories, Berkeley, California.

Upon elevated temperature, microscale and nanoscale features tend to coarsen, where larger features grow at the expense of smaller ones. This phenomenon has primarily been studied with respect to random distributions of particles. Recent experiments in patterned sapphire have suggested that preferred, coherent growth modes develop in uniformly sized features patterned on a square lattice. To this end, the linear stability of regular arrays of 3d particles coarsening in a 2d substrate is examined. The concentration field is considered under the point source/sink approximation. Numerical results from integrating rate equations will also be presented.

2:00 PM Q8.3

Statistical Mechanics: Undamaged <-radiation-> Damaged Atomic Lattice Density Evolution and Stochastic Deformation Functional. Ray B. Stout¹ and Natasha K. Stout²;

¹RhoBetaSigma Affaires, Livermore, California; ²Harvard School of Public Health, Boston, Massachusetts.

Radiation damage research of materials has a fifty year history[Kinchin & Pease]. The deformation kinematics for damage response of bulk materials is semi-empirical and phenomenological based on a continuum mechanics supposition: there exists a function space of continuous functions to describe material displacement, strain, strain-rate metrics by using the mathematics of differential calculus. Existing data assembled from tests on nano-length-scale(NLS) samples provide objective evidence that the continuum mechanics supposition is not an adequate generic mathematical description of damage response for surface-dominated material structures at NLS. Recent radiation damage analysis[Stout] used classical statistical mechanics concepts to define stochastic density functions for the number of undamaged, $N(x,t; q)$, and the number of damaged, $D(x,t; q)$, atomic lattices at spatial point x and lattice species q per unit spatial volume dx and per unit lattice species volume dq at time t . Boltzmann[1895] type evolution equations exist to describe the interdependent evolution of these two lattice density functions during radiation damage and damage annealing kinetics; as species of the $N(x,t; q)$ and $D(x,t; q)$ lattice density functions are destroyed and created during these two physical processes. The q lattice species variable contains physical attribute vector variables for the length dimensions of a lattice cell and time rates of the cell length dimensions for any lattice cell species. A relative deformation functional between two arbitrary spatial points is derived as a path integral functional. The integral functional depends on the stochastic lattice density functions $N(x,t; q)$ and $D(x,t; q)$. Using integral calculus mathematics[Shilov & Guerevich], path integrations can be evaluated over a countable stochastic set of arbitrary spatial paths. For a contiguous material, the vector measure of relative deformation exists as an invariant value independent of the physical spatial path between the two arbitrary spatial points. This path integral invariance is an analytical basis to statistically derive decomposition metrics for undamaged and damaged spatial sub-domains between any two arbitrary points. Variations in the spatial vector between two arbitrary points, by varying the position of one of the two points relative to the other, is an analytical basis to statistically derive length-scale metrics that are not in continuum mechanics models. These analyses address stochastic radiation damage evolution and will begin to illuminate physical enigmas and gray, shadowy representations of continuum mechanics at nano-length-scales. Boltzmann, L: 1895, Lectures on Gas Theory, trans. 1964 S. Brush, Un. of Cal Press, Berkeley. Kinchin, GH & RS Pease; 1955, Rpts on Prog in Physics, V-18, p3-33. Shilov, GE & BL Guerevich: 1977, Integral Measure and Derivative, Dover Press, NY. Stout, RB: 2004, Actinide Alpha-Decay in Spent Nuclear Fuels, rbsA Rpt 0010, Jun04.

2:15 PM Q8.4

The Effects of Synthesis Method and Particle Size on Doped Nano-TiO₂ and its Photochemical Activity.

Sherricka D. Daniel-Taylor¹, Timothy J. Boyle¹, Blake A. Simmons², Christina M. Baros¹ and Bernadette A. Hernandez-Sanchez¹;

¹Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; ²Sandia National Laboratories, Livermore, California.

The photochemical activity of organic contaminants has been widely studied using large bandgap semiconductors such as TiO₂, ZnO, and WO₃. However, there is a dearth of information regarding the doping of these materials with lanthanides or alkaline earth elements. Therefore, we are studying a science-based engineering approach to synthesizing active nanoparticles for decontamination applications given that prior research indicates there is a surface dominated phenomena at this size scale. Lanthanide (Pr, Tb, Yb) and Group 2 (Ca, Ba, Sr) doped titanium oxide (TiO₂) particles were prepared using a high temperature and pressure Parr Digestion Bomb or a methyl imidazole and water (MeIm/H₂O) method established in our laboratory. The particles were synthesized using lanthanide, group 2, and titanium alkoxide precursors. The resultant powders were characterized using transmission electron microscopy (TEM) which showed the particles to have sizes ranging from 2 – 200 nm, energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and experiments in which the degradation of methyl orange was monitored as a measure of photoactivity. The full synthesis, characterization and properties of the resultant nanoparticles will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

SESSION Q9: Degradation Processes in Nanostructured Materials

Chairs: John Baglin and Charles Hays
Wednesday Afternoon, November 30, 2005
Room 209 (Hynes)

3:30 PM Q9.1

Mechanical Properties of Electrophoretically-Deposited CdSe Nanocrystal Films. Shengguo Jia, Sarbajit Banerjee, Wei Wang, Ben Smith, Joze Bevk, Jeffrey Kysar and Irving P. Herman; MRSEC, Columbia University, New York, New York.

Approaches to measuring and then minimizing the strain and fracture in electrophoretically deposited CdSe nanocrystal films are investigated. Fractured films are seen for films thicker than a critical thickness, which depends on the size of nanocrystals (about 0.8 microns for 3.2 nm diameter nanocrystals). Cracks and some delamination are seen by SEM and AFM, and they are attributed to high strain energy in the film. This is thought to be due to the evaporation of residual hexane solvent after electrophoretic deposition - which changes the equilibrium separation of the nanocrystal cores. Photoluminescence and Raman microprobe scattering are used to investigate the stain distribution in nanocrystal film. Ways to minimize strain and to strength the films are investigated. These CdSe nanocrystal films become mechanically stronger and more resistant to chemical dissolution after being treated by cross-linker molecules such as 1,6-hexanedithiol, 1,7-heptanediamine and 2,2-biphenyldithiol. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award No. DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

3:45 PM Q9.2

Degradation of Copper-Silver Alloy Thin Films Induced by Annealing. Stephen T. Snyder and Alex King; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Copper/silver alloy thin films form with a fine, polycrystalline, metastable crystal structure. The expected effects of annealing include grain growth, transformation into the two stable phases, coarsening of the phases, texture formation, and the formation and growth of pinholes or voids. Copper/silver alloy films were deposited on single crystal sodium chloride substrates, via pulsed laser deposition ablation of a 66 Ag / 34 Cu [wt.%] alloy target, corresponding to the eutectic composition. Free-standing films of 20-30 nm thickness were studied as-deposited and after annealing at 100 Celsius for various times. Although several of the expected degradation processes involve short-range diffusion - essentially single atomic jumps - these were not observed, while other, longer-range diffusion effects were clearly identifiable. In particular, void shrinkage was observed in the films at short times, and void growth occurred at longer times. A simple study of the effects of several different contaminants was also conducted by performing annealing experiments using a variety of different TEM specimen grid materials to support the films.

4:00 PM Q9.3

Survivability of nanocrystal non-volatile memory transistors

in high-radiation environments: Experiment and modeling. Douglas Bell and Mihail P. Petkov; Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Electronics and detectors face unique challenges in high-radiation solar and planetary environments (e.g. the Jovian system). Intrinsic radiation tolerance for components such as non-volatile memory (NVM) is desirable in order to reduce the mass budget of external shielding. Nanocrystal silicon (nc-Si) floating-gate NVM transistors are expected to display greatly improved radiation robustness compared with conventional flash memory devices, due primarily to the distributed storage of bit charge in many isolated nanometer-scale storage nodes (the nanocrystals). It is expected that the radiation-induced loss of charge on a substantial fraction of the ncs may not necessarily lead to information loss (bit flip causing soft error). Nanocrystal floating gates are fabricated using several different methods. Si implantation into the SiO₂ gate oxide, followed by annealing, forms ncs with a statistical distribution of size and position. Aerosol deposition or direct growth of nanocrystals onto a tunnel oxide can produce a nc single-monolayer floating gate. We have previously reported total-dose exposure experiments on NVM test structures in which the nanocrystals were formed by implantation and annealing. Results show that the nc-Si NVM retains its memory function to a total dose of at least 15 Mrad. Characterization by electrical measurements and photoluminescence indicates that the nc-Si domains and the hysteretic memory effect remain largely unaffected by doses in this range. In order to apply these results to the optimization of nc-Si NVM robustness in high-radiation environments, we have modeled the nc-Si memory write and readout functions in the presence of ionizing radiation. Nanocrystals from 2-5 nm radius are placed into a floating gate array of nominal dimensions 100 x 400 nm. Both random distributions of nc within the gate oxide and regular close-packed monolayer nc arrays have been investigated. Injection of charge into the floating gate is simulated by uniform Fowler-Nordheim tunneling or by hot-channel injection, subject to coulomb blockade restrictions, with the potential throughout the structure calculated self-consistently during the charging process. After terminating writing at a selected time, and readout is performed by calculation of channel conductance and threshold shift due to the stored charge. Radiation-induced errors are simulated by modification of charge on ncs within the cross-sectional ionization area of a strike. Results on statistics of bit survival as a function of radiation characteristics and bit geometry will be presented.

4:15 PM Q9.4

Effects of Aqueous Environments on the Fracture of Nanoporous Organosilicate Thin-Film Glasses. Eric P. Guyer and Reinhold H. Dauskardt; Materials Science & Engineering, Stanford University, Stanford, California.

Nanoporous organosilicate thin-films containing controlled distributions of nanometer size pores are being developed for a range of emerging technologies. However, the materials are mechanically fragile and when exposed to moist or aqueous environments they are prone to environmentally assisted cracking. In this presentation, we demonstrate the significant effect of aqueous solution chemistry on accelerating crack growth in organosilicate nanoporous thin-films. We further show that the diffusion of aqueous solutions into films containing connected porosity can alter their stress state by changes in the surface stress of the internal surfaces. Using novel diffusion studies, we demonstrate the requirements for diffusion of aqueous solutions into these strongly hydrophobic films. The solution chemistry and presence of organic additions in the form of buffering agents significantly affects the ability of the solution to penetrate the nanoporous film. The resulting change in stress state has a profound effect on crack growth rate. For example, crack growth rates in acidic environments are accelerated by nearly an order of magnitude in the near threshold crack-growth regime while growth rates are inhibited by a similar amount in basic solutions. This behavior has important consequences for reliability since the growth of defects in device structures is particularly sensitive to the crack-growth threshold. Finally, implications for the integration of nanoporous thin-films into advanced devices are considered.

4:30 PM Q9.5

Ultrafast Laser Interaction with Nanostructured Epitaxially Related Ni/Ni₃Al Free Standing Thin Foils. Yoosuf N. Picard¹, Qiang Feng¹, Ben Torralva², Tresa Pollock¹ and Steven Yalisove¹; ¹Materials Science & Engineering, Univ. of Michigan—Ann Arbor, Ann Arbor, Michigan; ²Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Recent work in high intensity ultrafast laser interaction with free-standing, thinned single crystal Ni/Ni₃Al samples on the order of a 40 nanometers thick has shown a confinement of the mechanical and thermal effects induced by the incident laser pulse. Specifically, our work in the micron scaled machining of Ni-based superalloys with a

two-phase, single crystal structure has elucidated the high compressive shock wave such short pulsed lasers can induce. These materials consist of 600 nm sided cubes of the ordered alloy surrounded by 200 nm thick epitaxial Ni. This material has long range order and extremely low dislocation density, similar to a high quality Si sample. Through transmission electron microscopy, we have observed highly localized dislocation networks with significant densities within the area of laser irradiation. We have also observed very limited (less than 10 nm) melting along the edges of laser machined holes. We relate these observations of confined mechanical and thermal effects to the free-standing nature and limited heat conduction path of these thin foils when comparing to bulk samples. Hydrodynamic calculations will be presented that illustrate the issues surrounding the injection of dislocations into a thin foil.

4:45 PM Q9.6

Characteristics of The Oxide Layers Formed on Ge by Atomic and Molecular Oxygen Oxidation. Maja Kisa and Judith C. Yang; MSE, University of Pittsburgh, Pittsburgh, Pennsylvania.

Space vehicles residing in the low earth orbit (LEO) are exposed to various hazardous factors that can shorten their lifetime. LEO ranges from 200-700km in altitude from Earth surface, and the temperature varies between 200 and 400K. The most hazardous species in LEO is atomic oxygen having 5eV kinetic energy due to the high velocity of the spacecrafts (8km/s). Kapton is used as a structural component of the spacecrafts residing in LEO. Mass loss of unprotected polymer is very high in harsh LEO environment, primarily due to reactive atomic oxygen species. It is of primary concern to protect polymers in LEO from degradation, and nanometer scale coatings are used to accomplish this task. Germanium thin films are used as coatings to protect polymers from atomic oxygen attack, and to lower the solar cell operating temperature. The reaction of atomic oxygen with a protective coating occurs at the coating/oxide interface, at atomic level, thus indicating a need for using techniques capable of nanometer scale characterization. We previously investigated surface roughness, thickness, homogeneity, interface abruptness and oxidation states of several nanometers thick silica formed by exposure of Si(100) to 5.1eV atomic oxygen [1]. It was found that the amorphous silica formed by atomic oxygen was nearly twice as thick as the oxide created by molecular oxygen. The surface roughness of the oxide was increased due to reactive atomic oxygen. Oxidation of Si(100) in atomic oxygen produced more ordered oxide (similar to a quartz structure), and more homogeneous in composition. The Si/SiO_x interface formed by atomic oxygen was atomically abrupt, with no suboxides detected near the interface or throughout the oxide. We are planning to investigate and compare nanometer scale oxide films grown on Ge(100) at 493K by oxidation in hyperthermal atomic oxygen and molecular oxygen. Laser detonation source will be used to create hyperthermal atomic oxygen with kinetic energy of 5.1eV. This type of source creates atomic oxygen by using a pulsed CO₂ laser to detonate the oxygen gas to create an oxygen plasma, and this wave of atomic oxygen is neutralized and strikes the sample before re - combining into oxygen gas. Based on the same crystal structure of Ge and Si, we expect the effects of hyperthermal atomic oxygen on Ge oxidation to be similar to the effects of this reactive species on Si oxidation. Thicker, more ordered and on the surface rougher oxide is expected to be produced when Ge is oxidized in atomic oxygen. We forecast that the Ge/GeO_x interface will be sharp, with no suboxides. A variety of microcharacterization and surface science techniques will be used to study the effects of atomic oxygen on Ge oxidation. M. Kisa, T. K. Minton, and J. C. Yang, Structural Comparisons of SiO_x and Si/SiO_x Formed by the Exposure of Silicon(100) to Molecular Oxygen and to Hyperthermal Atomic Oxygen J.Appl. Phys., 97, 2005, 023520.

SESSION Q10: Nanomaterials and Ionizing Radiation
Chairs: Giuseppe Compagnini and Richard Wilkins
Thursday Morning, December 1, 2005
Room 209 (Hynes)

8:00 AM *Q10.1

Degradation of Polymers under Irradiation – an X Ray Photoelectron Spectroscopy Analysis. Jean-Jacques Pireaux, LISE Laboratory, University of Namur, Namur, Belgium.

Synthetic polymers are amongst the best scientific discoveries of the last century ; without them, our everyday life would be different. However, (some) polymers are not stable under light ; prolonged or energetic irradiation might induce chemical and structural and thus mechanical, electrical modifications. The aim of this presentation is to review the application of X-Ray Photoelectron Spectroscopy (XPS) in order to show its incomparable potentialities to unravel the elemental and chemical composition of polymer surfaces (core level analysis) and their structure (valence band analysis). XPS probing depth is in the range of nanometers... XPS is thus an unbeatable technique to

study surface and interface questions, like those involving surfactants, metal-polymer interfaces or UV degradation. Examples will be discussed like problems related to RF cold plasma treatment of polypropylene, or to UV excimer irradiation of polyethylene, polypropylene, and polytetrafluoroethylene.

8:30 AM *Q10.2

Ion Beam Patterning of Nanostructures. John E. E. Baglin, K10/D1, IBM Almaden Research Center, San Jose, California.

Fabrication of nanoscale patterned structures having high definition, robustness and reproducibility is uniquely appropriate for ion beam techniques. 2-D resolution of <60nm has previously been demonstrated for extended coherent patterns in Co/Pt multilayer magnetic media, using direct ion projection from a master stencil mask. 3-D features with high aspect ratio have been reported using an MeV proton beam writer. The use of patterned beams for lithography based on organic resists promises to out-perform e-beams or photon sources in terms of resolution, versatility and reliability. Application of these techniques to fabrication of master stamps for nano-imprint lithography seems highly attractive, but places further demands on the perfection and durability of the master. In this paper, we shall review the ability of ion processing to create nanoscale features of high performance, including such desirable feature properties as smooth boundaries and interfaces, physical stability, substrate adhesion, and resistance to thermal degradation or chemical corrosion under hostile conditions of processing or subsequent usage. In particular, we will show examples of high performance topographic patterns consisting of Si-DLC, derived by patterned irradiation of ALD layers of a polymer precursor.

9:00 AM *Q10.3

Effect of Metal and Metal Gas Hybrid Ion Implantation on Properties of Textiles Fabrics. Ahmet Oztarhan¹, Z. Tek², S. Selvi³, E. Oks⁴, I. G. Brown⁵, A. Nikolaev⁴, Selcuk Akturk⁶, Meral Saygun⁷, Altan Aksoy⁸, Oral Saygun⁹ and J. Sedef Gocmen⁸;
¹Bioengineering Department, Ege University, Bornova-Izmir, Turkey; ²Physics Department, Celal Bayar University, Muradiye/Manisa, Turkey; ³Physics Department, Ege University, Bornova-Izmir, Turkey; ⁴High Current Electronics Institute, Tomsk, Russian Federation; ⁵Lawrence Berkeley National Laboratory, Berkeley, California; ⁶Department of Physics, Kirikkale University, Yahsihan, Turkey; ⁷Department of Public Health, Kirikkale University, Yahsihan, Turkey; ⁸Department of Microbiology, Kirikkale University, Yahsihan, Turkey; ⁹Department of General Surgery, Kirikkale University, Yahsihan, Turkey.

In this work, mixed metal and gas ion beams were generated by MEVVA ion source and used to form buried layers of mixed metal-gas species to modify PES fabrics at an extraction voltage of 30kV and with various doses. An attempt was made to change the surface properties of PES fabrics by ion implantation of various ions without changing their bulk properties. Results showed that ion implantation causes an improvement of conductive properties and abrasion resistance, a decrease of friction coefficient, and changes of surface appearances of these fabrics. Flame retardancy, hydrophility, hydrophobity, pilling and antibacterial properties of ion implanted Cotton and Polyester fabrics were observed. The results showed that best flame retardancy of cotton was obtained when it was implanted with W+C ions where as the best flame retardancy of Polyester (PES) was obtained when it was implanted with C ions at a specific dose of 2x10¹⁵ions/cm². Hydrophility of PES was better found with low doses of C. It was found that Cotton fabric became hydrophob and its hydrophility decreased by a factor of 900 when implanted with W+C ions. The highest abrasion resistance of PES fabric was obtained with Ti+Al+N ion implantation. During the experiments ion charge state distribution were obtained with TOF. Implanting both sides of PES fabrics by Cu ions at an extraction voltage of 25kV and 1x10¹⁶ ions/cm² dose, prevented static electrification of PES fabric. Electrical conductivities of PES fabrics implanted with various substances were compared. Pb ion implanted PES fabrics with a dose of 10¹⁷ ions/cm² were exposed to the Pb210 radiation source(X & gamma rays) and it was found that there was about 6% reduction in the radiation through the Pb implanted samples. Anti bacterial study was conducted for evaluation of the affinities of two different bacteria (S.aureus ATCC:29213 and P.aeruginosa ATCC:27853) to PES fabrics implanted with various substances.

10:00 AM *Q10.4

Nanometric degradation of materials under swift heavy ions: can we extrapolate to low energy? Marcel Toulemonde, CIRIL, Caen cedex 5, France.

The state of art of nanometric amorphization of materials induced by dense electronic excitation following the slowing down of swift heavy ion will be presented (1-5). After a description of experimental observations and track quantifications, it will be shown that swift

heavy ions are very efficient to induce the phase transformations at a nanometric scale in many different materials. Special attention will be put on the different behaviors of the different materials. It will be shown that the inelastic thermal spike [3,6] could describe a lot of observations and can be extrapolated to low energy. The correlation between the nanometric observations and the chemical and physical properties of the irradiated materials will be described. We will focus in particular on the creation of tracks with magnetic properties, conducting tracks in insulators, nanoscopic change of the geometrical shape of material, lithography with high aspect ratio, etching of nanochannels suitable as templates for growth of metallic nanowires including multi-layer systems. [1] M. Toulemonde, S. Bouffard and F. Studer Nucl. Instr. Meth. B91(1993)108 [2] C. Trautmann, M. Toulemonde, K. Schwartz, J. M. Costantini and A. Mueller Nucl. Instr. Meth. B164-165(2000)365 [3] A. Meftah, J. M. Costantini, N. Khalfaoui, S. Boudjadar, J.P. Stoquert and M. Toulemonde to be published in Nucl. Instr. Meth. B [4] N. Khalfaoui, C.C. Rotaru, S. Bouffard, M. Toulemonde, J. P. Stoquert, F. Haas, C. Trautmann, J. Jensen, A. Dunlop to be published in Nucl. Instr. Meth B [5] A. Benyagoub Nucl. Instr. Meth. B225(2004)88 [6] M. Toulemonde, C. Dufour, A. Meftah and E. Paumier Nucl. Instr. Meth. B166-167(2000)903

10:30 AM *Q10.5

Formation, evolution and degradation of nanostructured thin films deposited by low energy cluster beam deposition.

Giuseppe Compagnini, Dipartimento di Scienze Chimiche, University of Catania, Catania, Italy.

Low Energy Cluster Beam Deposition (LECBD) is considered an intriguing technique to obtain thin layers with well defined structures at the nano- and meso-scale levels, allowing novel optical, electronic and magnetic properties. Atomic aggregates, formed by rapid cooling and seeded into suitable carrier gases, reveal exotic species which can be deposited retaining their properties because of the low landing energy on the substrate (0.1-1 eV/atom). The produced layers are highly porous and extremely reactive due to the high surface to volume ratio and must be characterized with in situ technique in order to study their original composition and their evolution once exposed to reactive gases. In this work we present a general overview and some results on the formation evolution and deposition of silicon and carbon cluster beams produced by a laser vaporization source. Silicon cluster assembled films are observed to retain their size features from the gas phase upon deposition and reveal luminescence in the visible and near-infrared, only if oxidized. On the other hand carbon clusters deposited at different temperatures are found to contain different electronic structures: some of them easily degrade upon annealing at room temperature or irradiating the sample by high energy particles.

11:00 AM Q10.6

Radiation Effects in Si Nanostructures. Gregory A. Kachurin¹, Svetlana G. Cherkova¹, Vladimir A. Volodin¹, Anton K. Gutakovskiy¹ and David I. Tetelbaum²; ¹SO RAN, Institute of Semiconductor Physics, Novosibirsk, Russian Federation; ²NIFTI, Nizhegorodsky State University, N.Novgorod, Russian Federation.

Effects of radiation environment and ion-beam/plasma technological treatments on the degradation of bulk semiconductors are widely investigated. Continuous downscaling of Si devices and the discovered visible luminescence of Si nanocrystals (Si-ncs) urge the study of the radiation effects in Si nanostructures. Here the effect of irradiation on Si-ncs in SiO₂ layers is reported. P, B and He ions of the keV energies and 400 keV electrons were used in the experiments. The samples were characterized by the photoluminescence (PL), Raman spectroscopy and HREM. Even individual atom displacements in Si-ncs were found to quench the PL, caused by the quantum-size confinement. The PL quenching rate depended non-monotonously on the elastic energy losses of the projectiles. At the same time HREM revealed an initial increase in Si-ncs number. Prolonged irradiation amorphized Si-ncs, even by the lightest particles, known to be unable to amorphize bulk Si. Recovery of partly damaged Si-ncs proceeds at annealing temperatures <1000°C. However the amorphized nano-inclusions need 1100°C anneals for re-crystallization, that is much higher than for amorphous bulk Si. The following interpretation is given. Due to the dramatically enhanced surface-to-volume ratio the crystal-matrix interface dominates the properties of Si-ncs. An initial increase in Si-ncs number is ascribed to the radiation-induced shock crystallization of nanoprecipitates, stressed by their surface shells. PL quenching by a single displacement points to the efficient fixation of the defects with formation of non-radiative recombination centers. When the elastic energy, transferred to Si atoms, is only slightly higher than the displacement threshold, the irradiation produces mostly the close Frenkel pairs, having high instant annihilation probability. PL degrades much faster, when the bombardment introduces well-separated components of Frenkel pairs. Further increase in the displacement cascade density causes partial

annihilation or binding of mobile point defects, thus hindering their sink to the interfaces. That explains the non-monotonous dependence of PL degradation on elastic energy losses. Because the Si-ncs surfaces readily capture the mobile defects, an amorphization by the point defect accumulation becomes possible. High crystallization temperature of the amorphized Si-ncs is attributed to a counteraction of their shells and to a low probability for appearance of the crystal nuclei in nanovolumes.

11:15 AM *Q10.7

Radiation Degradation of Nanomaterials for Power.

Ryne P. Raffaele¹, Cory Cress¹, Dan Brynes¹, Robert Walters² and Scott Messenger³; ¹Rochester Institute of Technology, Rochester, New York; ²Naval Research Labs, Washington, District of Columbia; ³SFA, Inc., Washington, District of Columbia.

We have been developing a variety of nanomaterials for their use in power devices. An example of this is our use of both single wall carbon nanotubes and several varieties of semiconducting quantum dots (e.g., CuInS₂, CdSe, InAs) for use in space solar cells. The ability of these materials to withstand the rigors of the space radiation environment will be essential for this intended application. In addition, we have also been developing both nanostructure III-V devices and radioluminescent quantum dots for use in radioisotope batteries. In this application, the nanomaterials are subjected to an extremely high radiation level. Their degradation rate will be the key to determining the ultimate lifetime of these power supplies, which in principle can have an energy density that is orders of magnitude higher than any conventional battery chemistry. The nanomaterials included in this study were subjected to electrons, protons, or alpha particles with the specific energy ranges and fluences determined by the intended application. A wide variety of analytical techniques have been employed to monitor the effects of radiation on the nanomaterials being developed including SEM, Raman and optical spectroscopy, photoluminescence, electrical conductivity. In addition, current versus voltage measurements of the nanomaterial-enhanced devices was performed as a function of irradiation. Results on the radiation tolerance of these nanomaterials and its implication with regard to their ultimately utility in power devices, based upon currently established theoretical modeling techniques, will be presented.

11:45 AM Q10.8

Degradation of Nano-crystalline ITO Films due to Exposure to Hyperthermal Atomic Oxygen. Long Li¹, Ross Harder², Ian K.

Robinson² and Judith C. Yang¹; ¹Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Spacecraft encounter a harsh environment in the low-Earth orbit (LEO), ranging from approximately 200 to 700 km, above the earth. The primary species in the low earth orbit are vacuum ultraviolet (VUV) radiation, and atomic oxygen, which is formed by the photodissociation of molecular oxygen, as well as electrons, X-rays and charged species. The high relative velocity between space vehicles and the ambient atomic oxygen (AO) leads to hyperthermal collisions of O atoms with spacecraft materials, with 5 eV kinetic energy. Indium-tin-oxide (ITO), a transparent conductive material, is typically employed as a coating material to protect Kapton blankets, used in solar arrays in LEO, from AO-erosion and static charge accumulation. 5eV hyperthermal atomic oxygen for the ground-based experiments was produced by the breakdown of molecular oxygen with a CO₂ laser. We used this atomic oxygen source to expose ITO films coated on float glass to investigate the mechanism of degradation of ITO by atomic oxygen. The starting ITO films had thickness of 150-200 nm with surface resistivity of 4-8 ohms. We characterized the surface of the ITO films before and after room temperature AO exposure with scanning electron microscope (SEM), synchrotron X-ray diffraction (XRD), and atomic force microscope (AFM). The ITO films were found to have a nano-crystalline surface comprised of round shape grains of 20-40 nm in diameter, and needle-like grains of 100nm long and 30 nm wide. Interestingly, SEM observation indicated that the morphology changes due to exposure were not localized at the film surface. The interface-sensitive peaks in XRD measurement with low grazing incidence also showed that changes occurred around the interface and the crystallinity of the ITO was modified. Since ITO is used as coating material to protect Kapton blanket from atomic oxygen erosion, our findings suggest that the atomic oxygen may react at the Kapton/ITO interface to enhance the delamination of the coating and thereby expose Kapton to rapid erosion with atomic oxygen.

2:00 PM *Q11.1

Degradation in Sn Films due to Whisker Formation.

Eric Chason¹, Gordon Barr², Lucine Reinbold¹, Vernorris Kelly¹, Paula Holmes², Jae Wook Shin¹, Wai Lun Chan¹ and K. S. Kumar¹; ¹Engineering, Brown University, Providence, Rhode Island; ²EMC Corp., Franklin, Massachusetts.

Thin films of Sn on Cu can degrade by the formation of whiskers, i.e., thin filaments of Sn that can grow to lengths of tens to hundreds of microns. Short circuits created by such whiskers have been implicated in the failure of a number of satellites and other commercial devices. Addition of Pb suppresses whiskering, but environmental regulations requiring removal of Pb from electronics have made it an urgent problem. Although the phenomenon has been known for many years, the mechanisms and driving forces for whisker formation are still not fully understood. A large body of data indicates that many factors contribute to their formation. Understanding their growth therefore requires understanding the interaction of multiple kinetic processes including interdiffusion, intermetallic formation and stress generation. To demonstrate how these processes interact, we will present measurements of the coevolution of stress, intermetallic formation, concentration profile and whisker growth made on well characterized thin film samples. Comparison of samples produced by vapor deposition and electrodeposition demonstrate the variability that can result from different processing techniques. Results on samples kept in ambient atmosphere or vacuum indicate the importance of the surface oxide and oxidation.

2:30 PM *Q11.2

Depressed Superconductivity at Oxides

Ferromagnet/Superconductor Interfaces. Jacobo Santamaria¹, V. Pena¹, Z. Sefrioui¹, D. Arias¹, C. Leon¹, N. Nemes², M. Garcia-Hernandez², S. G. E. te Velthuis³, A. Hoffmann³, M. Varela⁴ and S. J. Pennycook⁴; ¹GFMC. Fisica Aplicada III, U. Complutense, Madrid, Spain; ²Instituto de Ciencia de Materiales de Madrid (ICMM- CSIC), 28049. Madrid, Spain; ³Materials Science Division, Argonne National Laboratory, Argonne, 60439, Illinois; ⁴Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The need for smaller and faster electronics has motivated increasing interest in spintronic devices based on magnetoresistance (MR) effects associated to the accumulation and transport of spin polarized electrons. With the (re)discovery of colossal magnetoresistance (CMR) materials, there has been renewed interest in heterostructures involving oxide superconductors and CMR ferromagnets where ferromagnetism (F) and superconductivity (S) compete within nanometric distances from the interface. The high degree of spin polarization of the LCMO conduction band makes this system an adequate candidate for the search of novel spin dependent effects in transport. In F/S/F structures involving oxides, interfaces are specially complex and various factors like interface disorder and roughness, epitaxial strain, polarity mismatch etc., are responsible for depressed magnetic and superconducting properties at the interface over nanometer length scales. In this talk we will focus in F/S/F structures made of YBa₂Cu₃O₇ (YBCO) and La_{0.7}Ca_{0.3}MnO₃ (LCMO) showing that superconductivity at the interface is depressed by the combined effect of charge transfer, spin injection or ferromagnetic superconducting proximity effect. We will present experiments to examine the characteristic distances of the various mechanisms of superconductivity depression. In particular, we will discuss that the critical temperature of the superconductor depends on the relative orientation of the magnetization of the F layers, giving rise to a new giant MR effect which might be of interest for spintronic applications [1]. [1] V. Pena, Z. Sefrioui, D. Arias, C. Leon, J. L. Martinez, S. G. E. te Velthuis, A. Hoffmann and J. Santamaria, Phys Rev. Lett. 94, 057002 (2005). Work supported by MCYT MAT 2002-2642, CAM GR- MAT-0771/2004, UCM PR3/04-12399 Work at Argonne supported by the Department of Energy, Basic Energy Sciences, contract No.W-31-109-ENG-38

3:30 PM *Q11.3

Double Layer Processes of LBMO/YBCO and Crystalline

Degradations. Tamio Endo^{1,2}, Masanori Okada¹, Hidetaka Nakashima¹, Ajay K. Sarkar¹, Hong Zhu¹, Hirofumi Yamasaki² and Kazuhiro Endo²; ¹Electronics Engineering, Mie University, Tsu, Mie, Japan; ²NeRI, AIST, Tsukuba, Ibaraki, Japan.

Oxide microwave devices will be widely expected in mobile communication system in the near future in the world. Superconducting YBa₂Cu₃O_x (YBCO) thin films are most advisable for microwave filter devices due to their very low surface resistance.

Next generation devices are tunable microwave filters formed by double layers consisting of YBCO and ferromagnetic manganites such as La(Ba)MnO₃ (LBMO). In order to complete excellent double layers, we must first obtain proper techniques to fabricate perfect a/c-phases of YBCO and excellent crystalline LBMO single layers on substrate at low substrate temperatures (Ts), and then fabricate their double layers. We have tried an ion beam sputtering (IBS), then now we can control the perfect a-c orientation growths of YBCO. The minimum surface roughness is 1 nm for the c-phase and 0.3 nm for the a-phase. Excellent crystalline thin films of LBMO can be grown by IBS with controlling Ts, oxygen pressure (Po) and oxygen molecular or plasma supply on MgO and LAO substrates. It can be grown down to 480 deg C. The minimum rocking half-width is 0.01 deg, and the minimum surface roughness is 0.8 nm. As-grown LBMO film shows different metal-insulator transition and Curie temperatures. The results are interpreted by a phase separation and magnetostriction. The double layers of YBCO on LBMO and LBMO on YBCO were fabricated by IBS. In YBCO/LBMO, the excellent a/c-YBCO can be grown on the underlying LBMO at 600-650 deg C. The crystallinity of overlying YBCO is nearly the same with that of the single layers on MgO and LAO. The mosaicity of YBCO is much better than that of the single layers on MgO and LAO. It is noticed that the underlying LBMO crystallinity can be improved, and the mosaicity is not degraded after the double layer deposition. A deficiency is that the double layer surface is much degraded. Then we should fabricate the smooth underlying LBMO. In LBMO/YBCO, the excellent crystalline LBMO can be grown on the underlying a/c-YBCO at 650-700 deg C. The better crystalline LBMO grows on the better crystalline YBCO. The LBMO/a-YBCO clearly shows XRD peak separations while the LBMO/c-YBCO shows peak overlappings. The crystallinity of overlying LBMO is slightly poorer than that of the single layers on LAO. The mosaicity of LBMO is much poorer than that of the single layers of LBMO on LAO, but is almost the same with that of the underlying YBCO. It should be noticed that the crystallinity of underlying YBCO is degraded considerably after the double layer deposition. Then we should deposit the overlying LBMO at low temperatures. However a superiority is that the double layer surface is not degraded or rather improved. Now we are estimating time-dependence of the crystalline degradations on the single and double layers. YBCO crystallinity is easily degraded with time but LBMO is very stable. Then LBMO/YBCO is advisable in terms of a long term degradation.

4:00 PM *Q11.4

Superconductors in Confined Geometries. Zhili Xiao^{1,2}, Yew-San Hor^{1,2}, Jiong Hua^{2,1}, Umesh Patel^{2,1}, Yasuo Ito^{1,2}, Ulrich Welp^{1,2}, John Mitchell^{1,2}, Wai-Kwong Kwok^{1,2} and George W. Crabtree^{1,2}; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Northern Illinois University, Dekalb, Illinois.

When the dimension of a superconductor is reduced to the order of the penetration depth or the correlation length, its properties can change dramatically and become dependent on the boundary conditions imposed by the sample architecture. The synthesis of mesoscopic superconductors with well-controlled architectures is extremely challenging. I will present a brief review on the current status of research on mesoscale superconductors and highlight our efforts in synthesis and characterization of various mesoscopic superconductors. Our synthesized structures include nanoscale Nb antidot arrays and Pb nanowires fabricated through 'template synthesis', novel shaped Pb microcrystals grown with electrodeposition, and NbSe₂ and NbN nanowires/nanoribbons transformed from 1D NbSe₃ nanostructures. Physical characterizations of these superconductors yield commensurate effects, Little-Park oscillations, dissipation-induced granularity and other novel properties. The degradations of these mesoscopic superconductors were found and investigated systematically by measuring them at various exposure times to air.

4:30 PM Q11.5

Grain Boundary Diffusion in Nanocrystalline Electrolytes - Challenges and Opportunities. Scott J. Litzelman and Harry L. Tuller; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanocrystalline electroceramic materials promise increased ionic conductivity of solid electrolytes as the grain size approaches the Debye length and space charge regions begin to overlap [1]. Thus, nanostructured materials may have an impact in advancing sustainable energy conversion and storage technologies [2]. However, nanocrystalline electrolytes also present a potential challenge to stability, as the increased fraction of grain boundaries can act as short-circuiting diffusion pathways that can lead to device degradation. This effect can be enhanced in thin film electrolytes, which often possess a highly oriented, columnar microstructure with grain boundaries normal to the plane of the film. The kinetic properties and stability of several electrode materials, such as Ni, are

studied on CeO₂ thin films with grain sizes on the order of 20-40 nm. Samples were annealed in the temperature range of 300-700C, and diffusion profiles obtained by secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS). Large-scale diffusion of Ni into the ceria layer takes place at temperatures as low as 450C. Activation energies for the bulk and grain boundary diffusion coefficients are reported. Implications for device degradation are addressed. References [1] J. Maier, Solid State Ionics 154-155 (2002) 291-301. [2] A.S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, W. Van Schalkwijk, Nature Materials 4, 366-377 (2005)

4:45 PM Q11.6

Electrochemical stabilities of nanocrystalline and microcrystalline Cu deposits. Song Tao and D. Y. Li; Chemical & Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

Nanocrystalline materials have attracted increasing interest from tribologists and surface engineers due to their improved resistance to wear and corrosion. However, how the nanocrystalline structure affects the electrochemical behavior has not been fully clarified yet, since a nanocrystalline surface could behave differently when attacked by different corrosive media. Electrochemical properties of nanocrystalline and microcrystalline copper films with grain size ranging from 34nm to 2µm were investigated. The films were produced by pulse and direct current electrodeposition. This study was motivated by the fact that with increased applications of copper in the microelectronic industry, the surface stability and passivation behavior of this metal becomes more and more important. In this work, the grain size of coatings was determined using X-ray Diffraction and Atomic Force Microscope (AFM). The electron stability and chemical reactivity of the film surfaces were evaluated by measuring their electron work function (EWF). Corrosion behavior of the Cu electrodeposits was studied in various solutions, including NaOH, NaCl and H₂SO₄, using potentiodynamic polarization and electrochemical impedance measurements. The failure resistance of passive films developed in these solutions was studied by performing scratch tests with in situ monitoring changes in the contact electrical resistance. The study indicated that the grain refinement improved the passivation behavior; the passive film formed in NaOH were more protective than those formed in the NaCl and H₂SO₄ solutions; in particular, the passive film formed on nanocrystalline Cu in NaOH was stronger and more adhesive than that formed on microcrystalline one. However, in the NaCl and H₂SO₄ solutions, the nanocrystalline Cu surfaces were less resistant to electrochemical attack, compared to the microcrystalline ones. Such changes were expected to come from variation in the passivation behavior of copper in different solutions and could be explained based on the electron work function measurement.